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Groundwater Science Programme

Open Report OR/10/061

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A review of transport and attenuation of dissolved-phase volatile organic compounds (VOCs) in the unsaturated zone

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Summary

This report is concerned with transport and attenuation of dissolved-phase volatile organic compound (VOC) plumes in the unsaturated zone. The report reviews the international literature in this subject area, but emphasis is placed upon UK context and relevance. The review makes reference to, but does not critically evaluate how current understanding of VOC migration in the unsaturated zone is translated into practical risk-based assessment frameworks. It does, however, make observations as to the critical migration processes that should be considered in such frameworks to allow more effective knowledge-based decision making for the development of conceptual site models and the implementation of remedial actions appropriate to contaminated sites.

The key drivers for this review are the cost-effective management of VOC sources and associated contaminant plumes and the protection of groundwater. This requires an understanding and quantification of the processes by which the unsaturated zone offers protection to underlying groundwater resources from chemical releases at ground surface. Times taken for water to infiltrate and recharge the underlying water table may be long, possibly several decades where zones are thick. Furthermore, dissolved-phase chemical contaminants within infiltrating water may undergo attenuation and potentially be prevented from reaching the water table or delayed in arrival with much reduced concentrations present. A combination of processes including dispersion, sorption, volatilisation, chemical reaction and biodegradation may contribute to contaminant attenuation and protection of underlying aquifers.

The review is structured in eight sections, which comprise:

- Section 1, where the context, aims and objectives of the review study are described. In assessing VOC plumes in the unsaturated zone leached from shallow source zones it is important that: (i) understanding of transport and attenuation of chemical contaminants in the unsaturated zone is sufficient to both recognise and quantify the critical controlling processes; and, (ii) that understanding is translated into practical risk-based assessment frameworks to allow contaminated land problem holders, investigators and regulators alike to make effective knowledge-based decisions on remedial actions appropriate to contaminated sites. This report seeks to contribute to aspect (i) of this overarching goal.
- Section 2, which describes conceptual aspects of the transport and attenuation of dissolved-phase VOC plumes in the unsaturated zone that originate from near surface contaminant sources. A conceptual model is presented that forms the basis of the following sections, where the relevant underpinning process-based literature is discussed and the degree to which the conceptual model is quantified is considered. The processes that may influence the transport of dissolved-phase VOC plumes to the water table are categorised by three groups of processes: i) transport, ii) partitioning and iii) reactions. The section concludes that the volatile nature of VOCs adds significant complexity to classical leachable source zone models involving non-volatile contaminants. Furthermore, it recognises the importance of establishing the degree to which the conceptual model is quantified and the understanding of individual component processes and their interplay.
- Section 3 provides background on unsaturated zone water occurrence and movement in the unsaturated zone. It is recognised that percolation of water is non-steady and non-uniform and preferential flows may be anticipated at a variety of scales. Dynamic precipitation events, with infiltration pathways dependent upon previous climatic conditions and water saturation distributions throughout the unsaturated zone, add additional complexity to the prediction of actual water movement. The section concludes that although inevitable uncertainties in the water flow regime within the unsaturated zone will exist at a site, it is important that the understanding of water flow is maximised in order to provide more

confident interpretation of the VOC transport and attenuation superimposed upon that flow regime. Additionally, the anthropogenic nature of the contaminant source term may also cause the natural percolation of water to be significantly perturbed with the source potentially acting as a zone of enhanced or reduced recharge that has often varied over time as disposal facilities have changed from active receipt of wastes to becoming capped or abandoned.

- Section 4 considers the nature of the various shallow or partially penetrating VOC contaminant source zones that may give rise to dissolved-phase VOC plumes migrating in the unsaturated zone. The mass transfer processes of dissolution into infiltrating water and volatilisation into the gas phase that both control contaminant VOC transfer from the source zone to the wider unsaturated zone environment are also outlined. Consideration has been split between NAPL and non-NAPL sources with the latter subdivided to solid waste and aqueous-phase discharges. It is recognised that in practice, such segregation may not be apparent with, for example, isolated pockets of NAPL resident within a solid-waste deposit or NAPL droplets/residual within a liquid waste-stream. The section acknowledges that there may be many unknowns concerning the source zones that practitioners may face, including historical uncertainties such as the nature and timings of VOCs disposal, spatial complexities of the source zone and site investigation difficulties. These uncertainties need to be recognised in the assessment of dissolved plume infiltration through the unsaturated zone to underlying groundwater.
- Section 5 critically evaluates processes and factors controlling the migration of dissolved-phase VOC plumes through the unsaturated zone, including advection, dispersion, air-water partitioning (volatilisation), sorption, chemical reaction, biodegradation and plume transfer to the saturated zone. The variable presence of the air phase in the unsaturated zone causes all the above processes to be more complex than that encountered in the sub-water table saturated zone. Individual processes are described; however, it is clear that these processes are inter-linked, mutually influential and mutually occurring. The review identifies that that the transport and attenuation of dissolved-phase VOC plumes through the unsaturated zone has only rarely been the direct focus of research or practitioner study. This does not reflect a lack of importance of the subject, however, but more likely the technical and practical challenges inherent to addressing the problems of VOC migration in the unsaturated zone. The section concludes that the percolation of dissolved-phase plumes cannot be predicted, for example, without knowledge of the fate and transport of the vapour-phase VOC that may enhance or reduce the transport of a VOC plume to the underling water table. Biodegradation is recognised as a key process that may attenuate plumes, however, its potential applicability is governed by the potential of specific VOCs to biodegrade under the prevailing conditions that vary from being predominantly oxic to locally reducing where contaminant or electron donor loadings are significant.
- Section 6 evaluates our current capabilities to practically monitor unsaturated zone migration of dissolved-phase VOC plumes. The discussion does not explicitly address vapour phase or non-aqueous phase VOC sampling, which are beyond the scope of this review. The key challenges to acquiring representative samples of dissolved phase VOCs in the unsaturated zone include i) recovering samples from pore water that is either held in the pore matrix or is re-mobilised under gravity during recharge events, ii) minimising volatile and sorptive loss, in both sampling and preservation of VOC samples and iii) sampling at a spatial density that reflects the hydrogeological heterogeneity and contaminant distribution. The section concludes that whilst a coherent body of literature is available for vapour phase monitoring and non-aqueous phase sampling, it is apparent that sampling methods to assemble an equivalent evidence base for dissolved phase VOCs in the unsaturated zone is less mature, particularly in the area of in-situ sampling methodologies.

- Section 7 considers the fate of VOCs in fractured and dual porosity bedrock systems in the UK, particularly the Permo-Triassic sandstones that forms the second most important aquifer system in the UK and underlie some of its major industrialised areas. In addition to the processes described in Sections 4 and 5, diffusion-based transport dominates in the rock matrix, which is typified by slow migration velocities compared to advective transport in the adjacent fracture domains. The major features and processes relevant to transport through fractured unsaturated zones are illustrated by reference to an Idaho National Engineering and Environmental Laboratory INEEL) study. The INEEL work highlights the importance of considering the complete range of unsaturated zone processes, and their inherent complexities, when assessing solute migration in the unsaturated zone of fractured dual porosity bedrock systems. The section discusses the role of geological heterogeneity in controlling VOC distribution in dual porosity aquifers and concludes that uncertainty in the development of conceptual models to understand the spatial characteristics of VOCs may often be limited by sparse field evidence.
- Section 8 concludes the review and provides an overview of the knowledge gaps, uncertainties and research needs in the transport and attenuation of dissolved-phase (VOC) plumes in the unsaturated zone. Although much VOC research has been conducted in the unsaturated zone, there is a lack of studies that have specifically focused on the transport and natural attenuation of dissolved-phase VOC plumes infiltrating through the unsaturated zone. The review identifies that multi-scale experiments are required for the integrated assessment of simultaneously occurring processes that combine to influence plume migration. This research would permit key controlling processes and parameters to be determined, and quantified conceptual models built, that may underpin more robust practitioner tools. Specific recommendations for future research include:
    - Process understanding, including source terms, advection and dispersion, water/gas phase partitioning, sorption, aerobic and anaerobic biodegradation, and abiotic chemical reactions.
    - Analytical and numerical tools, in particular models that represent lower-strength source zone and tools that are accessible to practitioners.
    - Sampling methods, including the development of best-practice guidance in sampling methods that captures all four VOC phases (solid phase, non-aqueous phase liquid, aqueous phase and vapour phase) in the unsaturated zone.

The review demonstrates that the evaluation of contaminant migration through the unsaturated zone is non-trivial. There are both theoretical process understanding and practical site measurement challenges to face. Difficulties arise from trying to predict or measure the migration of contaminant through often complex and heterogeneous geologies containing both gas (air, vapours) and liquid (water, immiscible liquids, high particulate matter leachates) fluids. These complexities combined with a greater drive to understand contaminant migration in groundwater itself has led to understanding of contaminant migration in the unsaturated zone being generally less well developed with potential uncertainties in technical process understanding, monitoring capability, assessment frameworks and modelling tools.

The findings of this review are based on the research literature, practitioner evidence and case studies that were available to the reviewers in 2010. Research and practice in this field is constantly evolving and the reader is encouraged to consider the guidance in this document in conjunction with emerging literature, concepts and guidance.

Foreword

This report is the published product of a study by the British Geological Survey (BGS) and the University of Birmingham on the fate dissolved-phase volatile organic compounds (VOCs) in the unsaturated zone. The review provides a conceptual understanding of VOCs in the unsaturated zone, discusses processes that control the transport fate and transformation of VOCs in intergranular and fractured porous media, and explores knowledge gaps and research needs.

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1 Introduction

1.1 CONTEXT AND RATIONALE

Cost-effective management of contaminant sources and protection of groundwater requires an understanding and quantification of the processes by which the unsaturated zone offers protection to underlying groundwater resources from chemical releases at ground surface. Times taken for water to infiltrate and recharge the underlying water table may be long, possibly several decades where zones are thick. Further, dissolved-phase chemical contaminants within infiltrating water may undergo attenuation and potentially be prevented from reaching the water table or delayed in arrival with much reduced concentrations present. A combination of processes including dispersion, sorption, volatilisation, chemical reaction and biodegradation may contribute to contaminant attenuation and protection of underlying aquifers.

It has long been recognised that the unsaturated zone may serve to protect groundwater. Direct observations include the slow migration of nitrate from diffuse agricultural applications widespread over much of England's major chalk, limestone and sandstone sequences (Foster and Bath, 1983) and the gradual migration of leachate plumes from some 'dilute-and-disperse' landfill sites studied in detail, for example the Burntstump landfill on thick Triassic sandstone in Nottinghamshire (Lewin et al., 1992). Groundwater vulnerability assessment strategies and mapping (Environment-Agency, 2001) and groundwater protection strategies recognise the protective benefits of thick and, or low permeability unsaturated zones. Various groundwater legislation and regulatory policies, for example the citing of potential polluting activities such as septic tanks or waste management sites, also recognise the importance of the unsaturated zone and its attenuation properties in safeguarding groundwater supplies.

It is hence important that: (i) understanding of transport and attenuation of chemical contaminants in the unsaturated zone is sufficient to both recognise and quantify the critical controlling processes; and, (ii) that understanding is translated into practical risk-based assessment frameworks to allow contaminated land problem holders, investigators and regulators alike to make effective knowledge-based decisions on remedial actions appropriate to contaminated sites. *This report seeks to contribute to aspect (i) of this overarching goal.* Without such knowledge expensive remediation of sites may be needlessly undertaken, or alternatively remedial actions may not be implemented and aquifer - drinking water supplies exposed to unacceptable risk.

Evaluation of contaminant migration through the unsaturated zone is, however, non trivial. There are both theoretical process understanding and practical site measurement challenges to face. Difficulties arise from trying to predict or measure the migration of contaminant through often complex and heterogeneous geologies containing both gas (air, vapours) and liquid (water, immiscible liquids, high particulate matter leachates) fluids. These complexities combined with a greater drive to understand contaminant migration in groundwater itself has lead to understanding of contaminant migration in the unsaturated zone being generally less well developed with potential uncertainties in technical process understanding, monitoring capability, assessment frameworks and modelling tools. *The primary aim of this report is to critically review the status of knowledge and capability concerning transport and attenuation of dissolved-phase volatile organic compound (VOC) plumes in the unsaturated zone leached from shallow source zones.*

The focus on VOCs is warranted in that they have been found to be one of the most pervasive chemical groups encountered in aquifers impacted by urban – industrial sources and frequently found to have contaminated water supplies (Rowe et al., 2007). Since their widespread discovery in groundwater in the late 1970s onwards (Rivett et al., 2006), literally billions of dollars have been spent on their investigation and remediation across the developed industrial world and many legal actions brought to settle contentious cases of pollution. Primary groundwater

contaminant groups within the VOCs class are the aromatic hydrocarbons, for example BTEX (benzene, toluene, ethylbenzene and xylene) the primary toxic components of hydrocarbon fuels, and $C_1 - C_2$ (occasionally $C_3 - C_4$) chlorinated alkene/alkane VOCs typically referred to as chlorinated aliphatic hydrocarbons (CAHs) or else the 'chlorinated solvents' with respect to the parent solvent compounds used by industry such as TCE (trichloroethene) and PCE (tetrachloroethene) (Pankow & Cherry, 1996; Jackson, 1998; Rivett et al., 2005). Much attention has understandably been focused on the L/DNAPL (light/dense nonaqueous-phase liquid) behaviour of these VOCs as this critically controls their fate and transport in the subsurface with LNAPL often found to fully penetrate the unsaturated zone and accumulate on the underlying water table (Fetter, 1999), and DNAPL penetrate below the water table leading to residual and pooled DNAPL sources beneath the water table (Kueper et al., 2003).

Significant sources of VOC may nevertheless remain close to ground surface with an uncontaminated unsaturated zone still initially present that may afford protection to an underlying aquifer below. Such sources include not only small – medium quantities or widely dispersed releases of NAPL that fail to generate sufficient head to substantially invade the unsaturated zone, but also many predominantly NAPL-free sources including lagoons, pits and landfills (lined or unlined) receiving solids, sludges, liquid wastewaters rich in VOCs, soakaways, leaking sewers, septic – wastewater disposal points, leaking water supplies containing trihalomethanes (THMs). Leakage from and infiltration of water (natural precipitation or anthropogenic enhanced) through such sources and associated leaching may lead to the continual generation of dissolved-phase VOC plumes that may migrate through the unsaturated zone and contaminate underlying groundwaters unless attenuated.

1.2 AIMS, SCOPE AND APPROACH

The focus of this report is the transport and attenuation of dissolved-phase volatile organic compound (VOC) plumes in the unsaturated zone that primarily originate from near surface contaminant sources. Its overarching aim is:

- to critically review the status of knowledge and capability concerning unsaturated zone transport and attenuation of dissolved-phase VOC plumes.

This aim is primarily met via a literature review. The following objectives are identified:

- to identify the important processes and influential factors controlling the transport and attenuation of dissolved-phase VOC plumes in the unsaturated zone;
- to evaluate current site practice capability in assessing dissolved-phase VOC plume migration in the unsaturated zone;
- to identify knowledge gaps, uncertainties and research needs and associated prioritisation thereof.

The review aims to cover the international literature, but with emphasis placed upon UK context and relevance. The review makes reference to, but does not critically evaluate how current understanding of VOC migration in the unsaturated zone is translated into practical risk-based assessment frameworks. It does, however, make observations as to the critical migration processes that should be considered in such frameworks to allow more effective knowledge-based decision making on remedial actions appropriate to contaminated sites.

The approach taken is to:

- initially provide a conceptualisation and statement of the contamination problem studied (Section 2);

- provide relevant background on unsaturated zone water occurrence and movement (Section 3);
- consider unsaturated zone VOC source types and processes controlling the generation of plumes (Section 3)
- critically evaluate processes and factors controlling the migration of dissolved-phase VOC plumes through the unsaturated zone, including advection, dispersion, air-water partitioning (volatilisation), sorption, chemical reaction and biodegradation and plume transfer to the saturated zone (Section 5);
- evaluate our current capabilities to practically monitor unsaturated zone migration of dissolved-phase VOC plumes (Section 6);
- consider application to fracture and dual porosity bedrock systems in the UK, particularly the Permo-Triassic sandstones that underlie some of the UK's major industrialised areas (Section 0);
- identify knowledge gaps, uncertainties and research needs (Section 8).

2 Conceptualisation of the problem

2.1 INTRODUCTION

This section seeks to conceptualise the environmental issue, or 'problem', being addressed, namely the transport and attenuation of dissolved-phase volatile organic compound (VOC) plumes in the unsaturated zone that primarily originate from near surface contaminant sources and associated protection of underlying groundwater. The wider problem context is recognised and the section develops from consideration of the evolution of conceptual models of VOC contamination of groundwater to a schematic process-based conceptual model of the specific VOC issue under consideration. The conceptual model presented forms the basis of the following main sections where the relevant underpinning process-based literature is discussed and the degree to which the conceptual model is quantified is considered.

2.2 CONTEXT

The finding of widespread contamination of groundwaters by VOCs in the 1970-80s was initially met with some surprise as it was hitherto perceived that industrial or general urban losses of such volatile chemicals that included hydrocarbon fuels and industrial solvents would largely be to the atmosphere rather than subsurface. Clearly the observed contamination of aquifers indicated substantial amounts of VOCs were migrating through the subsurface unsaturated zone and entering underlying groundwater resources (Pankow & Cherry, 1996).

Conceptualisation of how VOCs may pollute groundwater chiefly evolved during the 1980s. Prior to that time groundwater pollution was largely conceptualised as the leaching of infiltrating precipitation of near, or at surface contaminant sources (e.g. contaminated ground, waste tip, or unlined landfill) to generate a dissolved-phase plume that would migrate through the underlying unsaturated zone down to the water table. Whilst this 'shallow leachable source' model is applicable to VOCs and is indeed the focus of this report, throughout the 1980s the importance of NAPL migration in the subsurface was recognised and NAPL conceptual models developed that were important to understanding the fate of VOCs as many of them are NAPLs in their pure form or used by industry within a NAPL form (Mercer and Cohen, 1990).

Whilst it had been hitherto reasonably appreciated that a spill of petroleum fuel (containing BTEX VOCs) may lead to accumulation of a pancake of hydrocarbon LNAPL on the water table (Fetter, 1999), there had been with perhaps occasional exception very little appreciation of the fate of dense organic liquids, i.e. DNAPLs, such as the chlorinated solvents in the subsurface (Rivett et al., 2006; Feenstra et al., 1996). The DNAPL conceptual model that developed from the pioneering work of Schwille and others indeed represented a paradigm shift in understanding (Mercer and Cohen, 1990; Mackay and Cherry, 1989; Schwille 1988). The potentially rapid migration of DNAPL completely through the unsaturated zone and accumulation of DNAPL potentially deep within the groundwater itself was subsequently deemed responsible for much of the widespread occurrence of chlorinated VOCs in groundwater observed from the 1970s onwards that still remains today (Pankow & Cherry, 1996; Rivett et al., 2005).

2.3 CONCEPTUAL MODELS

The development of dissolved phase VOC plumes in the unsaturated zone may result from a number of source zone scenarios, including disposal lagoons, landfills (lined or unlined) and point source releases (Figure 1). Elevated dissolved phase VOC concentrations may result from direct discharge of waste waters or from dissolution of L/DNAPL sources. Small to medium releases of NAPL that fail to generate sufficient capillary pressure to substantially invade the

unsaturated zone to depth, or where the vertical migration is limited by the presence of low permeability barriers, may remain as shallow sources that may be subsequently leached (dissolved) by infiltrating water. Where infiltration occurs, either directly through the unsaturated zone or through the waste materials in disposal facilities, a dissolved-phase VOC plume will evolve that may impact a significant thickness of unsaturated zone.

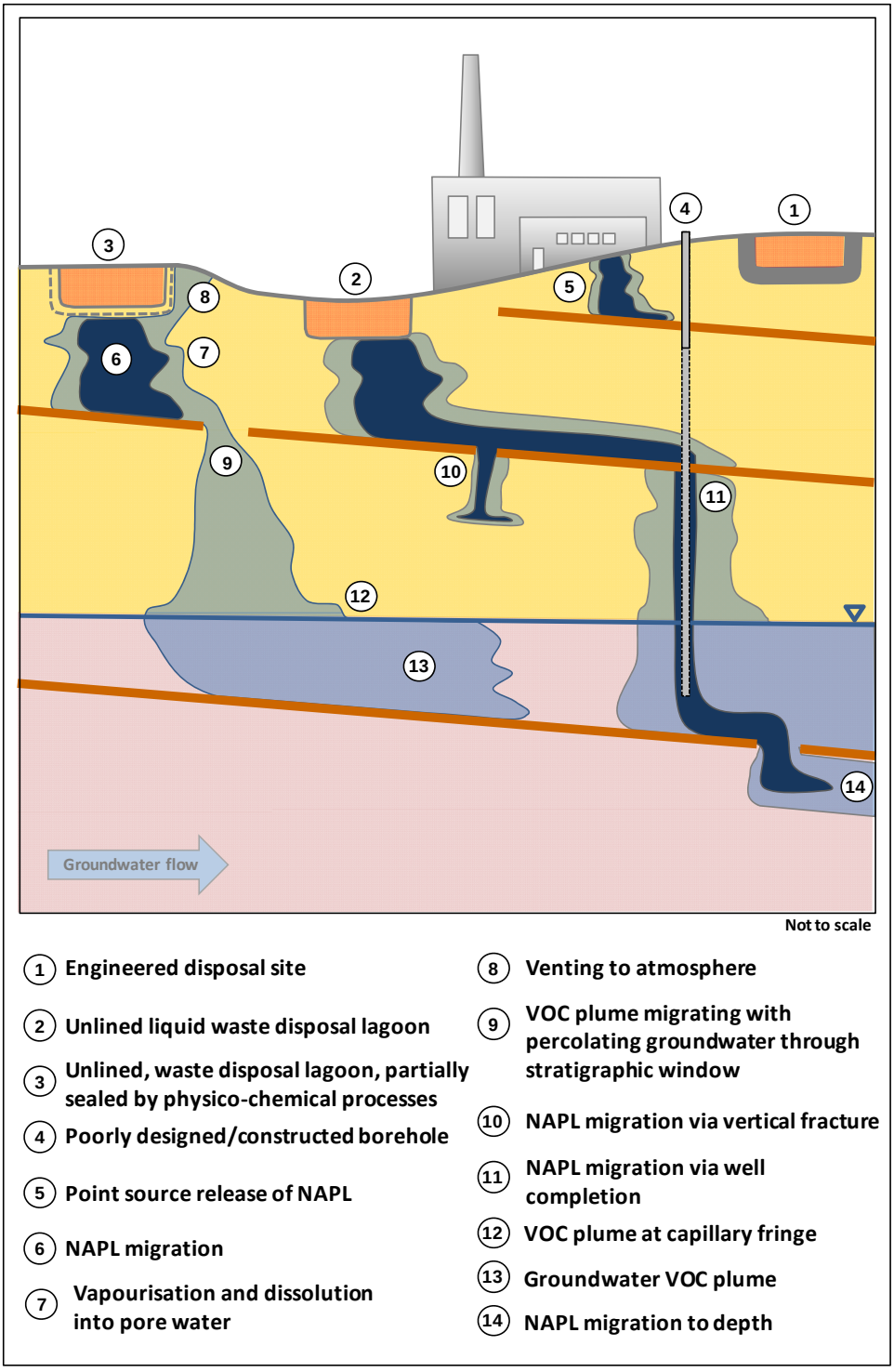

Figure 1. VOC conceptual model for multiple release scenarios.

Shallow leachable VOC sources are a relatively common phenomenon that may pose a substantial long-term environmental liability. The key drivers for understanding the impacts of shallow leachable NAPL source zones, or aqueous-discharge sources, on the unsaturated zone are the need to:

- to reduce uncertainty in prediction of timeframes for migration through the unsaturated zone that may range from hours to decades;
- to quantify the significance of the various natural attenuation processes that may retard or remove dissolved-phase VOCs and delay, or even prevent, arrival at the water table; and
- to facilitate development of appropriate risk assessment methodologies and remediation strategies.

2.4 PROCESSES INFLUENCING VOC TRANSPORT

Natural attenuation processes affecting the transport of VOCs in the unsaturated zone and their relative importance in controlling VOC transport may differ substantially between sites and depend, for example, on the modes of contaminant release, VOC properties, hydrogeological properties of the unsaturated zone, temporal factors (e.g. recharge and moisture contents). In summary, processes to consider that may influence the transport of dissolved-phase VOC plumes to the water table may be categorised by three groups of processes:

Transport

- Advection of dissolved-phase VOC plumes influenced by infiltration rates, water film connectivity, permeability and geological structure;
- Dispersion of dissolved-phase VOC plumes influenced by geological heterogeneity, anisotropy and fractured – porous nature (dual porosity) etc.;
- Diffusion of dissolved-phase VOC to low permeability zones or porous matrix adjacent to fractures;
- Transport and distribution of L/DNAPL that partially penetrates the unsaturated zone due to capillary forces and arresting low permeability horizons;

Partitioning

- Solubilisation (dissolution) of "solid" or liquid (L/DNAPL) VOC sources;
- Transfer to the air-phase through L/DNAPL vaporisation, or Henry's law partitioning from the dissolved-phase plume;
- Transport of VOC vapour plumes influenced by both diffusion and advection through the connected air-filled pore space and partitioning into infiltrating water or loss to the atmosphere;
- Sorption to geological solids and anthropogenic deposits present, for example high organic matter sludges in the waste deposited;

Reactions

- Abiotic chemical reactions, for example hydrolysis, nucleophilic reactions;
- Biotic reactions, i.e. biodegradation, mediated by bacteria.

These processes are reviewed in detail in Section 5 and follow underpinning understanding of water movement in the unsaturated zone (Section 3) and consideration of the various source terms and associated plume generation processes (Section 4).

2.5 RELEVANCE

The process-based conceptual model presented is illustrative of the complexity of shallow source types that may contribute to dissolved-phase VOC plumes percolating down through the unsaturated zone and the complexity and interplay of processes that may influence the transport and attenuation of that plume. The volatile nature of VOCs allowing co-existing vapour and dissolved-phase plumes adds significant complexity to classical leachable source zone models involving non-volatile contaminants. It is important to establish the degree to which the model is quantified and the understanding of individual component processes and their interplay. This will emerge from the sections that follow and consideration of the underpinning literature presented with variants. The conceptual model may serve to form the basis of conceptual site models (CSMs) developed by practitioners for specific sites. In view of the model complexity, identification and cost-effective quantification of the key controlling processes for the specific CSM would be seen as a priority practitioner need.

3 Unsaturated zone: Water occurrence and movement

3.1 INTRODUCTION

Understanding of water occurrence and movement within the unsaturated zone is critical to understanding VOC transport and attenuation in that zone. A contextual summary is provided below and the relevance to VOC transport summarised. The reader is referred to the more comprehensive texts cited for further detail.

3.2 WATER IN THE UNSATURATED ZONE

The unsaturated zone is the subsurface zone above the water table – capillary fringe with pores/fractures partially saturated with water and air present in the non water-filled porosity. Precipitation infiltrating the ground may percolate down towards the water table exerting a key control on the state of saturation. Temporal variation in precipitation, anthropogenic sources of water and climate generally causes the unsaturated zone to be in continual flux. Water is continually being absorbed, held or transmitted, either moving downwards towards the water table, or, at shallow horizons in particular, upwards towards the ground surface due to evaporation and evapo-transpiration where vegetation is present. Precipitation events can cause infiltration extremes. The unsaturated zone may become temporarily near fully saturated (pores water filled), with perched water tables occurring above low permeability horizons and lateral, rather than vertical, flows occurring locally. Conversely, during drought extremes, the unsaturated zone may become exceedingly dry with low moisture contents and high soil-moisture deficits.

The ability of unsaturated zone soils to retain and absorb moisture varies widely and is dependent on factors such as soil texture and structure. In general, coarser particles have larger interstitial voids and are responsive to infiltration, whilst fine-grained sediments like clays, are slower to absorb water, but also slower draining. Water is held in the soil by three main forces - capillarity, adsorption and osmosis (Ward and Robinson, 1989):

- *Capillary forces* result from surface tension at the interface between water and air. At these interfaces in soil pore spaces, the air will be at, or near atmospheric pressure, whilst the pressure of the water will be lower. As the water content of the soil decreases, the pressure difference increases and the interfaces become increasingly curved and water is held more tightly in the smaller pores or pore throats.
- *Adsorption* of water held in the soil occurs via electrostatic forces whereby polar water molecules are attracted to charged solid surfaces. Only thin films of water can be held around soil particles due to the weak forces, however, in clay soils of high specific surface area the overall volume of water held can be significant. Both adsorption and capillary forces exert a tension or suction force, combined they are referred to as ‘matrix suction’.
- *Osmotic pressure* influences water retention where differences in solute concentrations exist causing water to move across partially saturated pore space, from low to high solute concentration.

The relationship between pore water suction and soil moisture remaining in a soil is characterised by moisture characterisation curves (Ward and Robinson, 1989). Curve shape is related to pore size distribution, with largest pores draining at low suctions and smaller pores retaining water with air-water interfaces of greater curvature. Capillary forces are most important at lower suctions, whereas water retention occurs increasingly by adsorption at higher suctions. The use of moisture characterisation curves is limited, however, by their hysteretic nature

whereby the water content of a soil depends not only on suction value, but the previous moisture content (Lu and Likos, 2004).

Furthermore, transient wetting-drying-wetting sequences, which result in hysteretic moisture profiles, are observed to affect both the hydraulic conductivity and the residence time of solutes in the unsaturated zone (van Dama et al., 1996). Results from the analysis of hysteretic soil moisture profiles (van Genuchten, 1980) demonstrates that hydraulic conductivity in the unsaturated zone is a function of the wetting saturation, where higher saturation values were correlated with higher hydraulic conductivity.

The total soil water potential (ψ) can be expressed as (Ward and Robinson, 1989):

$$\psi = \psi_g + \psi_p + \psi_o \qquad \text{Equation 1}$$

where Ψg is the gravitational potential, Ψp is the pressure potential (comprising the matric potential above the water table and piezometric pressure potential below the water table) and Ψo is the osmotic potential (usually insignificant and ignored unless high solute concentration gradients exist). The gravitational potential acts to drain water from the soil downwards, whilst the pressure potential and osmotic potential act to draw water into the soil. Water flow occurs from areas of higher to lower potential energy and may be illustrated via an energy profile through the unsaturated zone (Figure 2). Upward flow is greatest near the surface where evapotranspiration is the dominant soil process and large matrix suction may develop. Downward flow due to gravity occurs deeper in the profile. Between these two opposing flow regions is the zero flux plane, the points of zero gradient on the total potential profile.

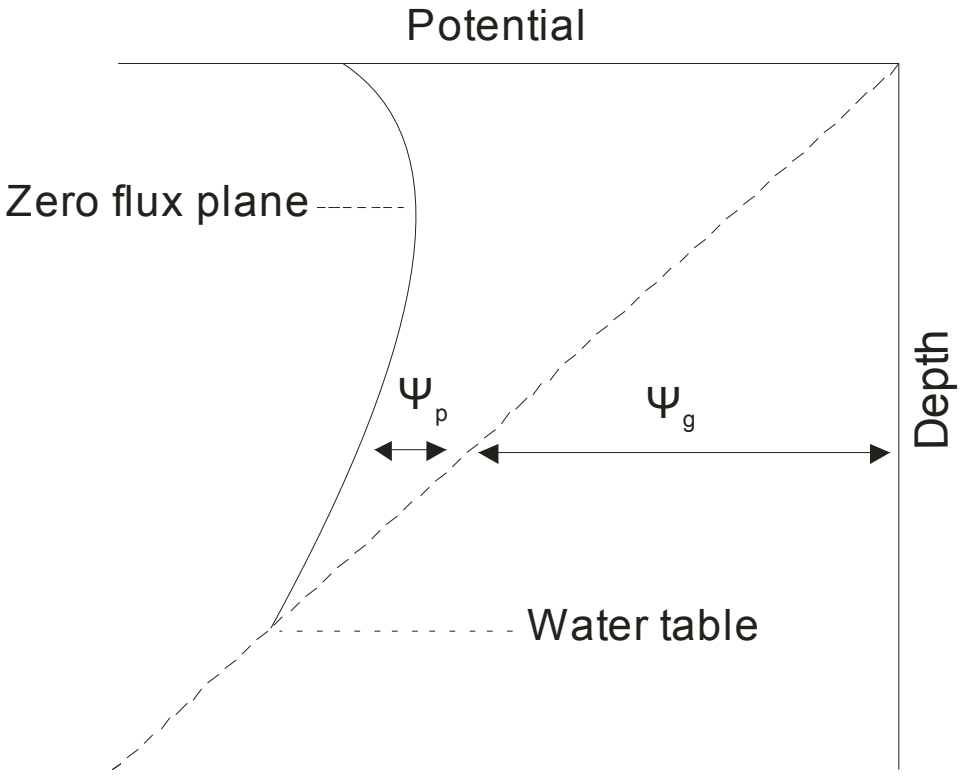

Figure 2. Total soil water energy profile (adapted from Ward and Robinson, 1989))

3.3 WATER INFILTRATION

A water infiltration event may induce substantial water movement in the unsaturated zone. As pores in the unsaturated zone are not fully saturated, the hydraulic conductivity and effective porosity are accordingly scaled down. With decreasing water saturation, hydraulic conductivity values decrease proportionately more than the effective porosity (van Genuchten, 1980). Thus, the downward velocity of water (and dissolved solutes) in a partially saturated porous media decreases rapidly relative to that if it were fully saturated. Quantitatively these processes may be expressed as below.

Unsaturated zone flow is typically described by the Richards Equation, a modified form of Darcy's law (Richards, 1931):

$$v = -K(\phi_w)\nabla i \qquad \text{Equation 2}$$

where v is velocity, K is hydraulic conductivity (varying with water content, ϕ_w) and ∇i is the hydraulic gradient (total potential versus depth). Information on moisture content is often more readily available, hence Childs and Collis-George (1950) introduced the term *soil water diffusivity* (D) to usefully relate flow to the gradient of water content (ϕ_w) instead of potential:

$$D(\phi) = -K(\phi_w)\frac{\delta\psi}{\delta\phi_w} \qquad \text{Equation 3}$$

Richards equation for flow further applies to typical field conditions where flow varies with space and time as in (Richards, 1931):

$$\frac{\delta\phi_w}{\delta t} = \frac{\delta}{\delta z}\left[K(\phi_w)\left(\frac{\delta\psi}{\delta z} - 1\right)\right] \qquad \text{Equation 4}$$

where t is time and flow is vertically downwards. The equation is only valid in uniform media and in steady-state conditions, where the gradient and flux do not change, or change very slowly over time. Hydraulic conductivity is a function of soil-water content and matric suction and decreases rapidly with reducing water content, which can change rapidly over time.

During infiltration of ponded water at surface, the unsaturated zone can be split into five zones (Figure 3). The saturated zone immediately below ground is a thin saturated layer of a few centimetres thick. Below is the transition zone, again a few centimetres thick, characterised by a rapid decrease in water content. In an idealised, homogenous system, the transmission zone has a near constant water content, but transmits the water from the top two zones to the wetting zone, another zone of fairly steep water content gradients. Over the course of the infiltration event, the wetting front (the division between wetted soil above and dry soil below) will advance downwards and the transmission zone will become elongated. Where ponded water at the surface is not present, the saturated zone and transition zone will be less pronounced.

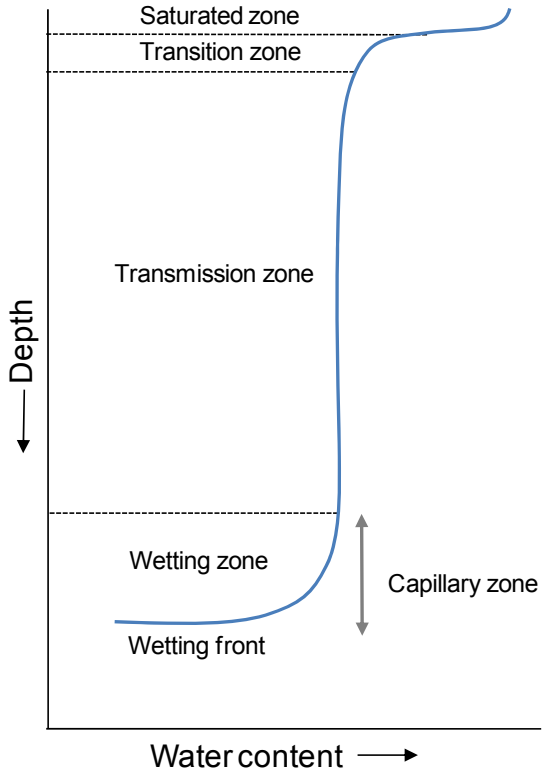

Figure 3. Moisture zones during ponded water infiltration into the unsaturated zone for a homogenous, non-layered system (adapted from Ward and Robinson, 1989).

3.4 CAPILLARY FRINGE

The capillary zone at the base of the unsaturated zone arises from capillary rise of water from the water table, or from the retention of infiltrating recharge. The zone in which capillarity keeps the pore spaces saturated, or nearly saturated is termed the capillary fringe. Capillary rise extends beyond this zone, but is restricted to movement through the films of water around soil particles. The velocity and direction of such movement is determined by the effective hydraulic conductivity (intrinsic van Genuchten parameters) and the gradients of matric suction and gravity. The extent of capillary rise is dependent on the texture of the matrix of the formation or soil. The former is important due to evaporation and transpiration creating the important suction forces which encourage upward movement through the soil, the latter controls the pore throat sizes, which directly affects the height of the capillary rise. As an example, chalk which is fine-grained (high porosity 20-45%, low matrix permeability $<10^{-2}$ m/d) will have a relatively large capillary rise (metre-scale), whereas the rise in unconsolidated gravels (high porosity 25-35%, high permeability ~10-20 m/d) would be much lower (e.g. cm scale). A table of capillary rise parameters was collated by Lu and Likos (2004) and were found to vary from 60 cm (Rewari sand) to 175 cm (Hissar sandy loam).

3.5 PREFERENTIAL FLOW

Water does not infiltrate through the unsaturated zone steadily and uniformly as may be assumed by many traditional models. Rather, preferential flow of water and associated transport of dissolved-phase solute in preferential flow domains is a major subject in its own right (Coppola et al., 2009 and papers in that issue). The reader is hence referred to that literature and a brief overview of salient points is made below. Gerke (2006) indicate “preferential flow comprises all phenomena where water and solutes move along certain pathways, while bypassing other volume fractions of the porous soil matrix”. Soils and the deeper unsaturated zone may exhibit heterogeneities at a variety of scales that may lead to preferential flows, for example in soils

small-scale heterogeneities may exist such as cracks, decayed root channels, inter-aggregate (or structural) pores and various macro- and coarse micro-pores. Discrete, contrasting permeability geological layers in the deeper sub-surface may act as preferential flow conduits such as fractures or fissures within a porous matrix (dual porosity) rock. The presence of sediment fills within fractures will alter the hydraulic characteristics of preferential pathways. However, the hydraulic conductivity contrast will be dependent on the fabric and consolidation of the sediment infill compared to that of the surrounding matrix (Hough et al., 2006; Wealthall et al., 2001).

Preferential flow may also occur due to not only obvious macropores, but also due to, for example, spatial irregularities or temporal dynamics in soil wettability, fingering due to instability of a wetting front and funnelling due to changes in the permeability structure of a soil (Sililo and Tellam, 2000; Coppola et al., 2009). These are dynamic, highly transient processes. Water infiltration through even relatively homogeneous porous media is only approximated by steady downward uniform flow. The process of fingering can cause this uniform plug to split into downward reaching fingers due to instability caused by pore-scale permeability variations. This occurs most frequently when a wetting front meets an interface of (marginally) coarser sediments (Hillel and Baker, 1988; Coppola et al., 2009). A further process, funnelling, is associated with discontinuous sedimentary layers across which infiltrating water may be funnelled along. When the infiltration water reaches the end of the funnel it will continue downward transport. This process can cause water to collect in certain locations (Kung, 1990) and the funnelling of water towards preferential flow regions (Vanderborght and Vereecken, 2007).

The geological heterogeneity and layering within most unsaturated zones is usually very significant and may lead to preferential flows occurring at various scales (Pan et al., 2009). Predominantly horizontal layering of (or slightly dipping) geologic layers may cause significant variations in hydraulic conductivity and porosity in a vertical profile through the unsaturated zone. The downward migration rate of an advancing wetted front (and NAPL) will be markedly influenced even by modest contrasts in conductivity and porosity. Fine-grained layers may reduce migration rates during prolonged infiltration and a perched water table may develop above the layer. Where a wetting front moves through a fine-grained layer into a coarser grained layer, the front may be slowed down. Although this appears to be counter-intuitive, the change is due to soil moisture suction at the wetting front which is too high to allow water to enter the larger pores of the coarser material. Such layering may induce horizontal flows. For example, Nimmo et al. (2002) reported evidence of horizontal flow at rates of >14 m/d, extending over 1 km in the unsaturated zone of the layered sediments and basalts at the Idaho National Engineering and Environmental Laboratory site. Layering and bed-scale geological structure may exert a major control as illustrated by the significant sub-horizontal displacement of the bromide plume injected in the lysimeter trench experiments in the Gardermoen delta aquifer, Norway where significant lateral tracer migration was observed to coincide with the direction of general geological dip (Søvik et al., 2002; Alfnes et al., 2004a)

Temporal variation in infiltration may also be significant alongside heterogeneity. For example, the modelling study by Jankovic and Andricevic (1996) evaluating the spatial and temporal distribution of recharge at the water table as a function of rainfall and heterogeneity predicts spatial non-uniformity of recharge dependant on soil heterogeneity that was most pronounced at the peak recharge when preferential flow occurred. During periods of low percolation intensity, the groundwater recharge was more evenly distributed.

Dual porosity aquifer systems, for example chalk, limestone and sandstones, may be characterised by preferential flows along fractures or fissures that may be orders of magnitude more conductive than the adjacent matrix. The importance of fracture flow is increased when infiltration occurs and the rate of water supply exceeds the infiltration capacity of the matrix pore space. This process may result in significant macro-scale hydrodynamic dispersion. During

fracture flow, water infiltration is likely to be anisotropic and hence not necessarily in the direction expected based on the potentiometric surface (Boulding and Ginne, 2004).

3.6 RELEVANCE

It is evident from this brief outline of water occurrence and movement in the unsaturated zone that migration of water from ground surface to the water table is a complex phenomenon. Although simple calculations of mean travel time of water may be made based on infiltration - recharge rates that give a typical downward percolation rates of perhaps c. <1 m / yr for example in the UK chalk (Rivett et al., 2007), the actual migration of water is a complex multiphase flow problem involving both air and water fluids set within heterogeneous unsaturated zones often of a dual-porosity nature. Percolation of water is non-steady and non-uniform and preferential flows may be anticipated at a variety of scales due to macropore features in soils, fingering and funnelling processes and controls exerted by geological layering predominantly normal to infiltrating flow. Dynamic precipitation events with infiltration pathways dependent upon previous climatic conditions and water saturation distributions throughout the unsaturated zone additionally cause the prediction of actual water movement to be impossible.

The transport of dissolved-phase VOC plumes down through the unsaturated zone is superimposed on the above complexities. The anthropogenic nature of the contaminant source term may also cause the natural percolation of water to be significantly perturbed with the source potentially acting as a zone of enhanced or reduced recharge that has often varied over time as disposal facilities have changed from active receipt of wastes to becoming capped or abandoned. Although it is recognised inevitable uncertainties in the water flow regime within the unsaturated zone will exist at a site, it is important that the understanding of water flow is nevertheless maximised in order to provide more confident interpretation of the VOC transport and attenuation superimposed upon that flow regime.

4 Unsaturated zone: VOC sources and plume generation

4.1 INTRODUCTION

The nature of the various shallow or partially penetrating VOC contaminant source zones, the 'source terms', which may give rise to dissolved-phase VOC plumes migrating through the unsaturated zone is outlined below. The mass transfer processes of dissolution into infiltrating water and volatilisation into the gas phase that both control contaminant VOC transfer from the source zone to the wider unsaturated zone environment are also outlined with the former of primary interest addressed in more detail. The understanding of the various source terms is important as it allows insight into the nature of the dissolved-phase plume that may develop in the underlying unsaturated zone and also the potential longevity of plume generation. At most sites a variety of source terms may exist as illustrated by the conceptualisation of the Hanford site in the US by Oostrom et al. (2007).

Consideration has been split between NAPL and non-NAPL sources with the latter subdivided to solid waste and aqueous-phase discharges. In practice, such segregation may not be apparent with, for example, isolated pockets of NAPL resident within a solid-waste deposit or NAPL droplets/residual within a liquid waste-stream. Source zone mass transfer considers not only dissolution into the aqueous phase, but also volatilisation into the vapour phase. The latter is important for VOCs and still relevant to dissolved-phase plume generation as migrating vapours can act as a source of pore water contamination via dissolution into the aqueous phase that is typically represented by a Henry's law partitioning approach. The transport of VOCs in the aqueous and vapour phases is covered in Section 5.

4.2 SOURCE TERMS

4.2.1 Solid-waste source zones

Solid waste disposal to land, i.e., landfill, has been a primary waste disposal route worldwide and includes both lined and unlined sites. Although the waste management excavation may have been purpose-built and potentially shallow, more often than not landfill of solid waste may have been to a former quarry, or mineral excavation sites. These are to varying and often substantial depths below ground, even below the natural water table where mineral extraction had been supported by dewatering. Many solid-waste disposal sites comprise both above and below ground storage of waste in order to maximise the waste deposited to a given land area.

The term "solid waste" is used in recognition that the waste comprises predominantly solid materials, for example contaminated soils/sediments, industrial-process sludges, filter-cakes, old chemical drums, metal shavings, redundant infrastructure, building rubble etc. The solid waste may, however, also contain liquid-phase and gas-phase material or contaminant. For example, industrial process sludges and contaminated soils/sediments may contain oil and solvent residues (perhaps as NAPL or emulsions) or contaminated wastewater within their pore space between the solids and old chemical drums may still contain liquid chemicals/waste. Chemical VOC liquid wastes (potentially as NAPL) may have been intentionally disposed of within the solid waste. For example, the practice of "co-disposal" of waste widely practised in the UK in its various forms prior to 2004 (when banned under the EC Landfill directive 1999/31/EC and associated legislation), may have used purpose-built trenches to infiltrate hazardous liquid chemical wastes into the mature domestic solid-waste landfill sites - a "bioreactor". Alternatively, chemical VOC liquid wastes (again potentially as NAPL) may have simply been indiscriminately dumped to a solid waste site as a very convenient means of simply getting rid of that material.

Although solid-waste disposal in developed countries is now tightly regulated in terms of the types of waste deposited, this was not the case prior to the *c.* 1960-80s (internationally and

locally variable) where there may have been comparatively little regulatory control over waste deposited in solid-waste disposal facilities (and still potentially is in some poorly regulated parts of the world). It should therefore be recognised that industrial waste-disposal sites, particularly those several decades old, may contain all manner of chemical or other wastes. It is also increasingly likely that older sites will not be lined (engineered) with an impermeable barrier placed below the waste (as in modern day practice) and plumes allowed to simply 'dilute-and-disperse' into the environment. Those sites of most relevance to VOC contaminant plume generation are those obviously in receipt of VOC-rich waste-streams. The disposal of used liquid industrial solvents or chemicals, often comprising individual or complex mixtures of VOCs, and their associated contaminated sludges and, or sediments is a primary contributor of VOCs to solid-waste sites.

4.2.2 Aqueous-phase liquid releases

Primary sources of aqueous-phase liquid releases (discharges) to the subsurface that may contain substantial concentrations of VOCs include waste(water) disposal lagoons, wastewater disposal pits, effluent soakaway systems, or shallow infiltration trenches or even wells. More secondary sources of aqueous-phase based VOC discharges to the subsurface include subsurface leaking sewers or pipework, septic – wastewater disposal points, leaking water supplies or chlorinated wastewaters containing elevated trihalomethanes (THMs). The focus herein is on the former, these being the principal industrial sources.

It is recognised, again that modern-day practice in developed and regulated countries is tightly controlled and disposal lagoons or soakaway systems previously allowed would now be banned. Older sites, operating or non-operating, are hence of primary concern. Modern-day sites, if permitted, would be better engineered – for example, a disposal lagoon may have a high specification liner and monitoring system installed to combat leakage to the subsurface. Older wastewater-disposal lagoon sites may be engineered to varying degrees. Some may simply be a fairly shallow excavated area with perhaps earthwork banks surrounding and a natural, unlined base that was anticipated to gradually leak to the subsurface thereby allowing continued input of the waste-stream. Although some sites may have recognised the underlying subsurface may have had some potential to "filter" the infiltrating contamination, many older sites may have simply given little, if any thought to the fate of liquids leaking from lagoon systems. Some lagoon or waste-water disposal points for toxic industrial waste-streams have been dev eloped in solid waste tips. For example coking – chemical – colliery works complexes may have piped liquid effluents to lagoons or pits excavated into existing mining spoil or solid-waste tips that had developed on sites. Such "toxic cells or lagoons" did have the benefit of the underlying spoil/tip artificial unsaturated zone to attenuate chemical before reaching the natural unsaturated zone below.

Although the descriptor used here is "aqueous-phase liquid releases", it is recognised to include wastewater effluents that may have very elevated solid/sediment and even potentially oil - NAPL contents that are perhaps better described as liquid slurries or sludges. These may have been piped to a lagoon disposal point to allow the solids to settle out and liquids gradually infiltrate the underlying subsurface. With time the disposal lagoon would have become filled with sediment and the disposal terminated. High liquid contents that may well remain in these wastes due to their fine sediment nature and high capillary retention usually dictate that they have poor geotechnical properties. Subsequent capping of waste by low permeability capping would hence be difficult meaning the waste lagoon may be left open to continued infiltration of precipitation and leaching long after disposal has terminated.

NAPL contents in some lagoons may also be quite high and should perhaps be considered as a NAPL source, at least in part. Examples include coking/gasworks type sites where phenolic tarry wastes may have been piped to lagoons. Although rich in heavyweight organics such as PAHs, they may still contain significant VOC fractions, e.g. BTEX. Again, convenient indiscriminate

dumping of liquid VOC chemical NAPLs directly to such lagoons may well have transpired, particularly historically.

4.3 NAPL SOURCE ZONES

The focus in this section is on source zones that develop in the unsaturated zone exclusively from the direct release of NAPL to the subsurface, either intentional or accidental. Many VOCs are used by industry as NAPLs and accidental spillages from tanks and storage facilities, leaking pipelines and drains were more likely until environmental controls improved in recent decades. Although there has doubtless been many illegal disposals of NAPL VOCs to ground worldwide, it is noteworthy that recommended disposal methods for many used chlorinated solvent VOCs up until at least the 1970s was to dispose of them by pouring on the ground, perhaps in pits and perhaps with ignition depending on other chemicals present (Pankow and Cherry, 1996). A combination of solvent volatilisation to atmosphere and infiltration to the subsurface would have occurred to varying degrees at disposal sites. The controls on L/DNAPL migration relevant to the formation of partially penetrating source zones in the unsaturated zone and the nature of the source zone formed is considered below.

4.3.1 NAPL migration and retention

L/DNAPL migration in the unsaturated zone is a multi-phase flow problem of significant complexity involving gas-, water-, and oil- (i.e. L/DNAPL) phases in a spatially complex subsurface porous and, or fractured medium with time-variant conditions (Kueper et al., 2003; Pankow and Cherry, 1996; Schwille, 1988). In the geological subsurface, water is usually regarded as wetting relative to the NAPL and the NAPL wetting relative to air. Unsaturated zone geological solids, even under quite dry climate conditions, are usually surrounded by a thin film of water. NAPL entering that media, will occupy the larger pores and pore bodies and be non-wetting on the solids with respect to water. On occasions where mineral grains are not coated with water, it is possible that the NAPL could be wetting with respect to water. This situation is less common, but is observed to occur after multiple NAPL spills (Powers and Tamblin, 1995).

Non-wetting NAPL is drawn downward through the unsaturated zone by gravity, but opposed by the capillary forces of the wetted geological media. For the NAPL to continue migrating, the pore ‘entry pressure’ must be overcome. Entry pressure is proportional to the interfacial tension and inversely proportional to the size of the pore throat. Hence, where apertures are small in fine-grained media, the non-wetting NAPL will only penetrate if the gravity force exceeds the pore entry pressure, which increases in direct proportion to the thickness of ponded NAPL on the interface (h). Prior to entry, the NAPL will accumulate and spread laterally above the geological interface. The critical height required for NAPL penetration (h_o) is estimated by:

$$h_o = \frac{2\sigma\cos\theta\left(\frac{1}{r_t} - \frac{1}{r_p}\right)}{g(\rho_w - \rho_{nw})} \qquad \text{Equation 5}$$

where σ is interfacial tension between the NAPL and water, θ is wetting angle, r_t is pore throat radius, r_p is pore radius, g is acceleration of gravity, ρ_w is density of water and ρ_{nw} is density of DNAPL, r_t is radius of the pore that NAPL must move through and g is force of gravity (Berg, 1975). If the NAPL was wetting with respect to water, the reverse would occur and capillary forces would enhance NAPL entry and draw NAPL into fine-grained media.

Movement of NAPL through porous media can be evaluated using a modified form of Darcy’s Law (Bedient et al., 1999):

$$v = -\left(\frac{k\rho g}{\mu}\right) i \qquad \text{Equation 6}$$

where v is Darcy velocity, k is intrinsic permeability, ρ is the fluid density, g is force of gravity, μ is the dynamic viscosity and i is the hydraulic gradient of NAPL mass.

NAPL, water and air are generally simultaneously present in the unsaturated zone that results in multiphase flow and competition for pore space and reduced mobility of individual fluids (Mercer and Cohen, 1990). The resulting permeability is termed the relative permeability and is the effective permeability of a fluid at a given saturation to the intrinsic permeability of the medium.

$$q_w = \frac{-kk_{rw}}{u_w}\left(\nabla P_w - \rho_w g \nabla z\right) \qquad \text{Equation 7}$$

$$q_{nw} = \frac{-kk_{rnw}}{u_{nw}}\left(\nabla P_{nw} - \rho_{nw} g \nabla z\right) \qquad \text{Equation 8}$$

where w denotes water; nw denotes NAPL; q is the volumetric flux (assumed positive down); u is the dynamic viscosity; ρ is the density; P is the pressure; k is the intrinsic permeability; and k_r is the relative permeability for each phase.

A trail of disconnected NAPL droplets (blobs) and ganglia will form in the pores (or fractures) of the unsaturated zone will be left behind the main body of NAPL infiltrating into the subsurface (Figure 5). NAPL invasion and drainage of the pore space is a hysteretic process that leads to discontinuous blobs and ganglia of NAPL being formed through snap-off of the gravity draining. The NAPL that remains is capillary-held immobile NAPL with the maximum capillary-held content being referred to as the "residual" NAPL saturation (S_n) that is a function of the subsurface geologic properties (e.g., pore/throat size), NAPL properties (e.g., density, viscosity) and their interaction (e.g., wettability) (Kueper et al., 2003; Pankow and Cherry, 1996). NAPL saturations may remain higher than residual saturation where the NAPL is pooled on a low permeability interface and there is insufficient driving force to overcome the pore entry pressure. Sensitivity of NAPL migration and retention to the geologic permeability field and varied air – water saturations present dictate that NAPL sources formed in the unsaturated zone will inevitably be spatially heterogeneous.

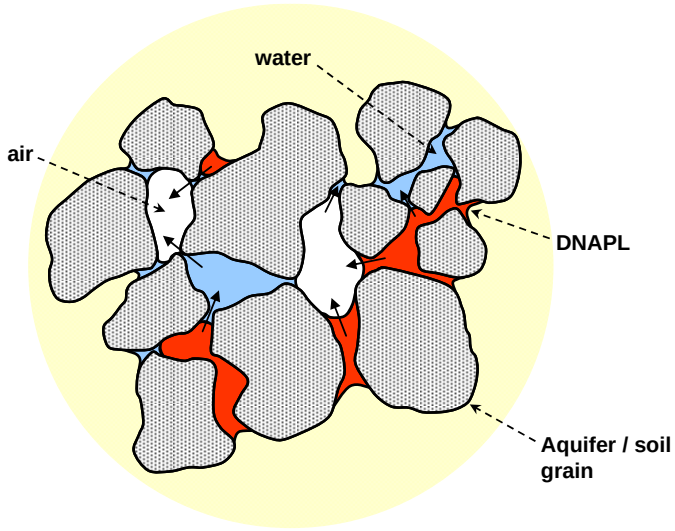

Figure 4. Conceptualisation of NAPL, air and water distributions in the unsaturated zone (solid arrows show possible VOC phase changes (Kueper et al., 2003).

4.3.2 Partially penetrating NAPL source zones

The controls on NAPL migration that may potentially lead to the formation of shallow, partially penetrating NAPL source zones in the unsaturated zone (thereby allowing the generation of a percolating dissolved-phase plume below them to be a concern and fitting the conceptual model in question; Figure 2) are summarised below.

There have been a number of studies (Acworth, 2001; Holzmer et al., 2005) that have examined the depths of penetration of NAPL, particularly DNAPL, into the subsurface, but not specifically into the unsaturated zone. There are many factors that control the depth of penetration meaning that precise prediction of such depths is very difficult (Wealthall and Lerner, 2000). Partial NAPL penetration of the unsaturated zone with predominant retention in shallower near-surface horizons would be increased by the following factors (relative phrasing is used to indicate parameter values towards the lower / higher side of typical parameter ranges etc.):

NAPL property factors

- NAPLs with lower density and higher viscosity leading to higher pore-entry pressures and higher residual saturations of NAPL in the unsaturated zone, e.g. viscous LNAPL lubricating oil will have less potential to rapidly and fully penetrate the unsaturated zone than a low viscosity DNAPL chlorinated solvent.
- NAPLs that are more non-wetting.
- NAPLs with greater vapour pressures that may cause greater mass loss to the vapour phase and potentially greater lateral spreading on subsurface entry (see the contrast in volatile DCM spreading relative to PCE in the experiments of Schwille(1988)).

NAPL release mode factors

- Smaller release volumes of NAPL
- Recent as opposed to historical releases, particularly where the NAPL is very viscous and low density and only migrates very slowly through the unsaturated zone
- A high release rate “catastrophic spill” that has sufficient head to invade a wider range of pore apertures in the shallow horizon relative to a gradual low release rate “drip” that may seek out a preferential discrete pathway and develop sufficient head to migrate to depth (see the PCE experiment at the Borden site by Poulsen and Kueper (1992)).
- NAPL released over a greater site footprint release area as opposed to a point release.
- Co-release with high water infiltration. For example, 2-D sand tank modelling of a scenario at the Hanford site in the US indicated DNAPL carbon tetrachloride could become trapped (occluded) by the large volumes of infiltrating water in the unsaturated zone (Oostrom et al., 2007).

Hydrogeological factors

- Geological units where capillary retention of NAPL is greater and (residual) saturations higher, e.g. less permeable high porosity media with small – medium pore sizes. It is noted, however, that in heterogeneous, temporally variable water saturated media that the movement and retention of NAPL is complex, a small change in permeability (and threshold entry pressure) may represent a significant barrier to migration and retention of NAPLs (Kechavarzi et al., 2008; Schroth et al., 1998; Wipfler and van der Zee, 2001).
- Greater occurrence of shallow laterally continuous (relative to the size of release) low permeability geologic units or layers on or in which NAPLs may pool or accumulate.

- An absence of transmissive pathways continuous to depth, e.g. high permeability gravels or course-grained porous media or high aperture connected fracture networks or palaeo-root channels.
- Lower water saturations in the unsaturated zone.
- Greater depth to water table.

It is clear from the variety of factors, prediction *a priori* of the depth of migration of a NAPL in the unsaturated zone is very difficult, if not impossible. Even with detailed site investigation, e.g. coring, the degree of partial penetration of NAPL is difficult to estimate with confidence because the borehole examines such a small percentage of the medium, and the DNAPL distribution is typically very heterogeneous. Nevertheless, the above listing offers pointers to when shallow, partially penetrating NAPL sources are more probable.

The above range of factors controlling penetration of NAPL in the unsaturated zone would also infer that the source zone of L/DNAPL formed in the shallow unsaturated zone will be highly variable. The spatial distribution of NAPL is likely to be highly heterogeneous with varying depths of partial penetration through the unsaturated zone governed by largely the geologic permeability field. The exception would be if a continuous low permeability unit had largely prevented penetration leading to an extensive accumulation of NAPL at that interface. Subsequent preferential dissolution or vapourisation of NAPL in more permeable horizons may be quite variable due to preferential mass transfer from the more permeable horizons leading to increasingly patchy, isolated NAPL zones developing with time at pore and greater geological spatial scales.

Peak NAPL residual saturations in the unsaturated zone are generally 10 - 20% of pore space (Mercer and Cohen , 1990). At the very local scale within many NAPL spills it is probable that NAPL is completely absent within parts of the subsurface beneath the spill. Thus volume averaged saturations over the larger scale of a spill zone may be much lower than peak residual saturations. For example, Poulsen and Kueper (1992) observed an average residual saturation in the unsaturated zone of just 1.26% (over the general spill zone) for a ponded instantaneous release and just 0.49% for a slow drip release of PCE in the fine-medium sand Borden aquifer, Canada. There is a need for more measurements in different lithologies and varying conditions, e.g. water content, spill history, spill area (Oostrom and Lenhard, 2003).

4.4 SOURCE ZONE MASS TRANSFER

The various VOC source terms that may occur in the unsaturated zone have differing capacities to generate dissolved-phase plumes that may migrate down through the underlying unsaturated zone. Of critical influence to the generation of infiltrating dissolved plume, of primary interest, is the co-occurring process of volatilisation that allows simultaneous mass transfer from source zones into the gas phase as well as dissolution into the infiltrating aqueous phase. The nature of the volatilisation process is initially outlined in order to provide context to the discussion of mass transfer from the various source terms and generation of leached plumes in the sections that follow.

4.4.1 Volatilisation

VOC volatilisation to the vapour phase allows mass transfer from the source zone additional to dissolution that is a result of the inherently volatile nature of VOCs. The VOC vapour plume formed may remain in that gas-phase ‘soil gas’ and be potentially lost to atmosphere at ground surface, or else re-incorporated to percolating water (Mendoza and McAlary, 1990) where upon it may still become part of the unsaturated zone dissolved-phase plume. High saturated vapour pressures of VOCs (that are markedly temperature dependent) may cause elevated vapour concentrations in pores or fractures immediately adjacent to a NAPL source, particularly for the more volatile, lower boiling point, VOCs. Although vapour plumes may be associated with

solid-phase landfill or lagoonal effluent disposal points, volatilisation from NAPL sources generate the most significant vapour plumes due to the high VOC mass inherent in such sources and ready partitioning across the NAPL – air interface.

The equilibrium vapour phase concentration immediately adjacent to a single component NAPL VOC is given by the saturated vapour pressure (P_o) of the VOC. Although all VOCs are volatile the range in volatility is large spanning over an order of magnitude, for example, a P_o value for PCE of 0.02 atm compares to a dichloromethane (DCM) value of 0.46 atm (at 20 ^oC). Saturated vapour pressures and hence vapour concentrations adjacent to NAPL sources are sensitive to temperature variation. VOC vapour pressures increase by around 30% for a change in temperature from 0 - 25ºC (Pankow and Cherry, 1996). Such a temperature range may occur at shallower horizons, to about c. < 5 m. At greater depths, temperatures may be expected to be more constant, at around 11ºC.

Partitioning to the gas phase may also occur via water / air partitioning of dissolved-phase VOCs in the aqueous phase. At equilibrium, concentrations in the adjacent phases are described by a VOC's Henry's law coefficient (H) (dimensionless):

$$H = \frac{C_g}{C_w} \qquad \text{Equation 9}$$

where C_g and C_w are the equilibrated concentrations in gas (air) and water respectively (with similar concentration units). Like vapour pressures, Henry's Law coefficients exhibit both significant range across the various VOCs and, importantly, significant temperature dependence (Staudinger and Roberts, 1996, 2001). As an equilibrium constant, the temperature dependence of H has been found to be adequately modelled by a van't Hoff-type equation. For data correlation, a generalised form of the traditional van't Hoff equation is typically used and Henry's law constant as a function of temperature (H_T) may be expressed as (Staudinger and Roberts, 2001):

$$\log H_T = A - \frac{B}{T} \qquad \text{Equation 10}$$

where A (-) and B (Kelvin) are simple curve fitting parameters and T is the temperature (Kelvin). Staudinger and Roberts (2001) summarise data from 55 studies that measured H_T in dilute, non-saline aqueous solutions over a temperature range 0-40 ^oC. Staudinger and Roberts use Equation 10, H_T data from these studies and the corresponding enthalpy of volatilisation, to determine and report A (intercept) and B (slope) temperature dependence relationships for a wide range of organic compounds including many VOCs. They report an average B value of 2145 K (all organic compounds) that corresponds to an average increase in H_T by a factor of 1.88 (i.e., an 88% increase) per 10^{o}C rise in temperature, with the range of percent increases being from 12 to 255% per 10^{o}C rise. Some example A / B values and percent increases per 10^{o}C rise are: benzene 5.053 / 1693K for 60%, ethylbenzene 6.541 2100 K for 79%, trichloroethene 5.874 / 1871 K for 68%, and vinyl chloride 4.119 / 1223 K for 40%. Numerical simulations of vapour transport by Thomson et al. (1997) for TCE indicate such differences may be significant in the shallow subsurface environment prone to temperature fluctuations.

Mass transfer across the water / gas interface and NAPL / gas interface (and NAPL / water interface (Section 4.4.4)) may be recognised to be rate limited (i.e., phases are not at equilibrium) and mass transfer theory (borrowed from the chemical engineering literature) has been used to characterise the various parameters affecting mass transfer rates. Lumped parameter first order mass transfer rate expressions for (Henry's) water / gas partitioning, NAPL

volatilisation and NAPL dissolution have been adopted defining lumped parameter first order water / gas partitioning dissolution (λ_H), volatilisation (λ_V) and dissolution (λ_D) rate coefficients (1/T) (Sleep and Sykes, 1989, Thomson et al, 1997; Jang and Aral, 2007). Thomson et al. (1997), for example, define the source/sink term for the gas phase (Γ_g)as follows (with the parallel water term given in Section 4.4.4):

$$\Gamma_g = \emptyset S_g \lambda_v \left(C_g^m - C_g\right) - \emptyset S_g \lambda_H \left(C_g - HC_w\right) \qquad \text{Equation 11}$$

where ϕ is the total porosity, S_g is the gas saturation (of porosity), C_g and C_w are the mass concentration of VOC in the gas and water phases respectively, C_g^m is the maximum concentration of VOC in the gas phase.

Hence the dissolution (or leaching) of VOCs into the aqueous phase will be significantly influenced by the concurrent NAPL – gas volatilisation and water / gas partitioning processes.

4.4.2 Solid-waste source zones

The generation of dissolved-phase VOC plumes from solid-waste sources, for example old unlined landfills, is primarily dependent upon the potential for infiltration of water through the waste material and contact with and leaching via dissolution of VOC-contaminated material within that waste body into infiltrating water. With time, the quantity of VOC source material will decline and leached concentrations reduce. However, in wastes where VOC quantities are high and, or percolation rates are low, this decline may be very slow and it essentially functions as a semi-infinite source of contamination potentially lasting decades or longer. In the cases where there are relatively low quantities of VOC contaminated waste, it may be anticipated that contact of percolating water may lead to sporadic, spatially variable elevated concentrations leaching from the footprint of the landfill. Extraneous NAPL may not be entirely absent from such wastes and where present may be expected to yield hot-spot elevated VOC concentrations, particularly where the NAPL is rich in an individual VOC. From a practical standpoint, the spatial distribution of VOC emanating from the areal base of a landfill is likely unknown due to the monitoring difficulties (accessibility constraints). It is hence difficult to directly measure or predict with confidence contaminant mass flux from the base of a source term.

Attenuation of VOC concentrations may be significant within the waste body, particularly if the waste has a high sorption capacity and, or biodegradation capacity and VOC fluxes from this source term to the underlying unsaturated zone may be significantly reduced. Co-disposal of organic industrial wastes, potentially rich in VOCs into mature domestic waste that was methanogenic was based on this principal and the waste body being a significant bioreactor (Reinhart et al., 1991). Other solid industrial waste streams may also facilitate sorption of VOCs on to fine particulate solids of high surface area and, or organic matter contents. Likewise, biodegradable (oxygenated)-hydrocarbons, and other electron donors/acceptors, deposited may facilitate the biodegradation of more recalcitrant organic contaminants such as chlorinated VOCs that mostly degrade under anaerobic reducing conditions which are promoted by the availability of electron donors. Elevated concentrations of some organic contaminants, e.g. cis-1,2-dichloroethene (Slusser et al., 2001) and some metals, e.g. mercury, may, however, lead to toxicity effects and inhibition of biodegradation (Sandrin and Maier, 2003).

Variation of water infiltration through the waste body critically controls the VOC flux discharged from the base of the waste and the source term longevity, which will reduce with greater flushing rates. The capping of unlined landfills with low permeability caps is a key control measure that may lead to much reduced water percolation and leachate fluxes from the waste. The downside is that the waste may persist as a source term for decades longer due to substantially reduced flushing. Sites that remain uncapped will continue to act as a contaminant source to the unsaturated zone with their longevity determined by the quantity of source mass

and flushing rates. It is also common that unlined sites filled with waste may be more permeable than the surrounding consolidated natural ground and act as a focal point for recharge, potentially further exacerbated if sites are located in a topographic depression and, or permeable strata supporting perched aquifers that intersect and drain into the waste. Fluid fluxes may hence be substantially increased through the underlying unsaturated zone and mounding of the underlying water table occur (MacFarlane et al., 2003). The indiscriminate disposal of wastes into geological voids that naturally focus recharge such as 'swallow holes' is particularly undesirable.

VOC concentrations in water percolating from the base of a solid waste source zone equate to the concentration in the dissolved-phase plume entering the unsaturated zone, the plume input concentration (C_0). C_0 could perhaps be measured in a water or leachate sample collected from the base of the waste material, however, monitoring accessibility is challenging and extraction of capillary-held pore water may result in VOC volatilisation losses. Alternatively, a soil sample total VOC concentration may be measured (as pore-water extraction is difficult), and the pore water VOC concentration determined from air-water-soil phase-partitioning relationships. These, for simplicity, typically assume linear, reversible equilibrium partitioning and K_d (soil-water partitioning coefficient) and H (Henry's Law constant partition coefficient) apply. Mass balance between the solid, aqueous and air phases within the sample (or an unsaturated zone domain) is assumed and the total soil chemical concentration (C_t) (μg/g dry weight) is given by the partitioning relationship that is routinely used in contaminated soil risk-assessment (and more sophisticated) models (Griffin and Watson, 2002) and provided by Feenstra et al. (1991):

$$C_t = \frac{K_d C_w \rho_b + C_w \phi_w + C_w H \phi_g}{\rho_b} \qquad \text{Equation 12}$$

which may be rearranged to give the chemical concentration in the pore water (C_w) (mg/L or μg/cm^3):

$$C_w = \frac{C_t \rho_b}{\left(K_d \rho_b + \phi_w + H\phi_g\right)} \qquad \text{Equation 13}$$

where ϕ_w is water-filled porosity (volume fraction), ϕ_g is gas (air) filled porosity (volume fraction), ρ_b is dry bulk density of the soil sample (g/cm^3), K_d is the partition coefficient between pore water soil solids (C_s / C_w) (cm^3/g), C_s is chemical concentration sorbed on the soil solids (μg/g dry weight) and C_g is chemical concentration in the soil gas (mg/L or μg/cm^3).

The calculated C_w value may be equated to C_0. Although such equilibrium partitioning approaches may be a simplification of reality, they nevertheless provide a convenient first approach to quantitatively consider simple partitioning of VOCs between the soil – water – air phases. They may be applied to not just soil samples, but also to the determination of VOC mass distributions between phases anywhere in the subsurface contaminated domain. It is noted that the above mass balance equations as written do not consider any mass that may be present as NAPL in the sample. The presence of NAPL would, however, be potentially revealed if a C_w value was calculated that exceeded the solubility of the VOC, or effective solubility for VOCs in a multicomponent NAPL (Section 4.4.5).

4.4.3 Aqueous-phase liquid discharges

Waste (water) or effluent disposal lagoons have often received wastewater effluents containing elevated solid/sediment and, even NAPL contents as liquid slurries or sludges, many of the issues raised for the solid-waste sites apply. Additionally, during the active deposition phase water (or other liquids) are actively being discharged to the lagoon surplus to precipitation and

will maintain a driving head for fluid entry to the unsaturated zone. The head differences and permeability of the lagoon waste-sediments relative to the surrounding natural deposits will primarily influence the leakage of contaminated waters to the subsurface during operational phases.

Layering of lagoon sediments is likely significant and vertical permeability to water flow reduced where significant thicknesses of fine sediments are present. A crust may form at surface, particular post disposal that may also cause ponding and increased evaporation or run-off. Lagoons in receipt of significant quantities of co-disposed DNAPL may have leaked DNAPL through the facility base and walls. Typically the geotechnical stability of lagoon or tip waste is such that specialised equipment is required to access the waste body and make reliable measurements of the flow regime through a lagoon and generation of dissolved-phase plumes into the unsaturated zone below. Expense typically precludes such being routine and sites are heavily reliant on perimeter monitoring that may give a poor or even misleading impression of the source term.

Soakaway style effluent discharges to ground are chiefly characterised by their flow rates and the distribution of the discharge to ground. Often, however, flow rate information can be poor, in that historic records can be completely lacking and there can be reliance on nominal or authorised discharge amounts rather than actual observed data. Percolation through the unsaturated zone is clearly greatest when the discharge was active. Discharges that have terminated may, however, still be problematic years to decades later when percolation rates are low and, or unsaturated zones are thick leading to a slowly migrating body of contaminated water to the water table.

In some cases of aqueous-phase liquid discharges to ground, determination of a source zone C_0 concentration may perhaps be trivial and simply involve measurement of VOCs in a water sample collected from the discharge. There may, however, be cases where estimation of C_0 is much more problematic. For example, access to the discharge point may not be possible, the discharge was historical and VOC concentration data were not collected, the liquid sample contains significant solids that potentially interfere with VOC analyses, or else volatilisation losses to atmosphere occur from an open lagoon surface or high velocity discharge point that need to be considered.

4.4.4 NAPL source zones

The presence of NAPL in any of the unsaturated zone source types is important as its simultaneous volatilisation into the air phase and dissolution into infiltrating water may lead to very elevated concentrations in both the vapour and leached aqueous-phase plumes that develop. Concentrations may approach saturated vapour pressures or solubility values where volumes of released NAPL are significant. The substantial NAPL dissolution literature (see below) has almost exclusively assessed dissolution in the saturated zone. Unsaturated-zone VOC NAPL mass transfer studies at the lab or field-scale have focused instead on volatilisation and vapour plume migration process as these are often thought to be the dominant process and key in the consideration of contaminant risks posed to receptors at ground surface (Bouchard et al., 2008 amongst many others). Systematic evaluation of simultaneous unsaturated-zone NAPL dissolution and volatilisation appears to be restricted to modelling studies (Sleep and Sykes, 1989, Thomson et al, 1997; Jang and Aral, 2007).

Field research studies on NAPL volatilisation have generally covered NAPL sources to remove the additional complication of dissolution (Christophersen et al., 2005; Conant et al., 1996). Field or lab studies focusing on dissolved-phase plume generation arising from water percolation through unsaturated zone NAPL sources appear largely absent from the literature with minor exception. For example, the study of Bohy et al. (2006) provides some limited insight. They emplaced a TCE-PCE NAPL source in the unsaturated zone of the 3 m deep (2 m unsaturated zone), 12 m wide, 25 m long artificial aquifer SCERE facility. Infiltration was, however, only

allowed for 6 hr over a >80 d experiment period largely concerned with vapour transport. Sampling of the aqueous-phase was restricted to the underlying capillary fringe some distance below the infiltrated source and hence data on the dissolution process were limited. VOC vapour concentrations were observed to decline after water was infiltrated with four days necessary for the recovery of vapour concentrations. The decline was attributed to VOCs partitioning into the relatively clean water. The impact of water infiltration on the dissolved-phase VOC concentrations in the capillary fringe was predicted to be more significant in model simulations than observed in practice. This was tentatively attributed to a lack of instantaneous equilibrium between phases during and immediately after the infiltration when the advective downward transport rates where highest.

The numerical models that have considered simultaneous volatilisation and dissolution by infiltration of water use first order mass transfer rate expressions for both NAPL dissolution and volatilisation defining lumped parameter first order dissolution (λ_D) and volatilisation (λ_V) rate coefficients (1/T) (Sleep and Sykes, 1989, Thomson et al, 1997; Jang and Aral, 2007). The parallel sink/source term to the gas phase given earlier (Section 4.4.1) for the water phase (Γ_w) expressed in terms of first order relationships is (Thomson et al., 1997):

$$\Gamma_w = \emptyset S_w \lambda_D (C_w^m - C_w) + \emptyset S_g \lambda_H \left(C_g - H C_w\right) \qquad \text{Equation 14}$$

where S_w is the water saturation (where $S_g + S_w = 1$) and $C_w{}^m$ is the maximum (solubility) concentration of VOC in the water phase. The depletion of mass from the NAPL source may then be given by (Thomson et al., 1997):

$$\Gamma_w = \emptyset S_w \lambda_D (C_w^m - C_w) + \emptyset S_g \lambda_H \left(C_g - H C_w\right) \qquad \text{Equation 15}$$

where ρ_n is the density of the NAPL and S_n is the NAPL saturation.

Such first order rate constants (Equations 11, 14, 15) are dependent upon many physical parameters, including pore velocity, interfacial surface area, pore scale geometry, geologic heterogeneity and the degree of residual NAPL saturation (Thomson et al., 1997). Sleep and Sykes (1989) did not have relevant values from the literature to constrain the values of λ_D, λ_V (and λ_H – Henry's Law rate coefficient), but rather varied the values of these rate coefficients from 0.0 to 0.5 in their transport sensitivity analysis. They note the potential to quantify rate constants by inverse modelling using concentration and flow data from lab or field experiments. It would appear that such observed data remains a critical lack. Jang and Aral (2007) in fact do not cite any experimental rate coefficient literature and simply define all rate coefficients as being 1.0 d^{-1}. There hence remains a need to undertake controlled lab and field studies on simultaneous dissolution and volatilisation of NAPL sources in order to validate the above models and provide more robust descriptions of unsaturated-zone NAPL source depletion by both mass transfer processes.

Of the above numerical modelling studies, the work of Thomson et al. (1997) provides the most thorough examination of the sensitivity of simultaneous NAPL dissolution and volatilisation to various factors, notably variation in mass transfer coefficients, NAPL source depth interval, surface cover changes and seasonal variations of infiltration, temperature and surface cover to which the reader is referred for details. This and the other modelling studies typically consider a 2-D section that is around 16 m deep and 400 m long with the upper 5 m or so unsaturated and the NAPL source a little below ground surface, around 0 to 2 m depth. Hence the mass transfer from the source is considered within the wider scenario context. The work of Thomson et al. allows the mass transfer rates for dissolution (including direct dissolution of NAPL and also

VOC partitioning (dissolution) from the gas phase into infiltrating water) and volatilisation to be assessed with time alongside rates for VOC water/gas partitioning and diffusion loss to atmosphere.

In their base case scenario for a TCE source of residual saturation 25% all values of λ_D, λ_V and λ_H were all set equal to 1.0 d^{-1}. Relatively steady-state mass transfer rates were shown for 50 – 1000 d after an initial period of high rates driven by high concentration gradients. Volatilisation from the NAPL at steadystate was c. 400 g/d slightly above the dissolution rate of 300g/d. However, the rate of water / gas VOC partitioning was comparable to dissolution with diffusion into the atmosphere attained a rate of some c. 670 g/d (comparable to the sum of volatilisation and dissolution) with little VOC entering groundwater below (c. 20 g/d). The sensitivity analysis of Thomson et al. (1997) that builds upon the base case is informative. For example, setting rate coefficients to 1000 d^{-1}, to simulate equilibrium dissolution, volatilisation and water/gas partitioning, did not allow steadystate to be reached due to the rapid source depletion, but achieved mass transfer rates 5 times the base case, including a 5-fold greater loss to atmosphere and negligible input to groundwater below. Cases that examined examples where dissolution or volatilisation rates were decreased or removed, lead to other mass transfer rate correspondingly increasing. However, similar groundwater accumulation and atmospheric losses were still observed regardless of these rates and attributed to the coupling between the aqueous phase and the gas phase. This result implied that both the aqueous and gas phase plume concentrations derived from a NAPL source are most sensitive to the water / gas partitioning rate. Mass transfer rates from the source will also be influenced by vapour density effects as density-driven advection allows high concentration vapours to be advected downward from the NAPL residual allowing lower gas concentrations within the source. Thomson et al.'s (1997) simulations indicate they act to increase the rate of VOC partitioning from the aqueous phase to the gas phase, and subsequently, to increase dissolution rates.

Thomson et al., however, illustrate that moving the 2 m thick source zone incrementally closer to the water table at 5 m depth causes dissolution rates to increase with increasing water saturation and volatilisation and water / gas partitioning rates to decline due to the decreasing. With a source just on the water table, TCE accumulation in groundwater occurs at a rate of 220 g/d (an order of magnitude greater than the base case) with diffusion to atmosphere and water / gas partitioning rates at c. 60 g/d and volatilisation just 4 g/d. Dissolution rates deeper in the unsaturated zone do in fact decrease relative to the near surface base case though as gas-phase diffusion from the source directly to the atmosphere is decreased. This causes higher gas phase concentrations near the NAPL that decrease the water / gas partitioning rate thereby inhibiting dissolution. As Thomson et al. (1997) note, when considering the range of uncertainty in determining NAPL source location in the unsaturated zone, the fate of VOC contamination (i.e., to atmosphere or groundwater) appears to be much more sensitive to source locality than to the range of mass transfer coefficients discussed above.

The literature for single process (as opposed to simultaneous) NAPL mass transfer, either NAPL dissolution or volatilisation, is contrastingly vast and may be used to provide some insight. For example, the dissolution literature expected to be most applicable where water contents approach saturated conditions (and vice versa for volatilisation). Both literatures demonstrate: the potential for equilibrium saturated aqueous-phase or vapour-phase concentrations when NAPL saturations or contact times are high; kinetic rate-limited concentrations at low contact length to velocity ratios, or when NAPL-water interfacial areas are low; and, the importance of source zone and geological heterogeneity causing pathways through sources that effectively by-pass discrete zones of NAPL within the bulk source (e.g., the dissolution literature - Seyedabbasi et al., 2008; Zhang et al., 2008; Rivett and Feenstra, 2005; Powers et al., 1994; Imhoff et al., 1993). Understanding of the various physical parameters (listed above) that control first order rate has largely emerged from such literature. This literature includes extensive laboratory, intermediate scale, field and modelling work. Studies of simultaneous dissolution and volatilisation mass

transfer are, however, still required to validate the numerical models already built and discussed above.

High spatial variability of dissolved-phase plume concentrations emanating from NAPL source zones is often considered probable due to the significant spatial heterogeneity of most real NAPL sources. The complex source zone 'architecture' typically comprises disconnected ganglia, blobs and pools that accumulate on low permeability media. Water flowpaths through source zones may variously contact NAPL, with some pathways potentially not contacting NAPL at all, particularly if dissolution fingers propagate through the source with time (Rivett and Feenstra, 2005). Percolation through the unsaturated zone may cause flow perpendicular to the layered geology that results in different NAPL interactions and dissolution to that observed in the saturated zone. NAPL accumulated on low permeability strata may perhaps be better flushed.

Although the architecture of NAPL in the unsaturated zone is invariably poorly constrained, it should be appreciated that any NAPL present may cause long-term plume hotspots within due to the elevated VOC mass present within a NAPL. From a practitioner perspective, any data that can be gained on NAPL location is hence valuable. Such data may include records of possible NAPL disposal areas and timings and the results of targeted source zone investigation. Soils, aqueous-phase and vapour-phase source zone, or other (e.g. geophysical) data may all contribute to delineating the possible presence of NAPL hot-spots.

4.4.5 Multi-component NAPL source zones

Many NAPLs used by industry are in fact mixtures of compounds and typically referred to as multi-component NAPLs. Examples include hydrocarbon oils and fuels, solvent blends and used (spent) solvents that contain organic greases and oils. The key difference between single and multi-component NAPLs is that the 'effective solubility' of individual components within multi-component NAPLs is reduced due to the presence of the other components. The effective solubility, C_s^i, of component *i* in the aqueous phase is given by (Mackay et al., 1991):

$$C_s^i = X_n^i \gamma_n^i C_o^i \qquad \text{Equation 16}$$

where C_o^i is the aqueous solubility of component *i* as a pure compound and X_n^i is the mole fraction and γ_n^m the activity coefficient of component *i* in the NAPL mixture. If ideal solution behavior is assumed, activity coefficients become unity (Broholm and Feenstra, 1995) and the C_s^i expression simplifies to an analogue of Raoult's law:

$$C_s^i = X_n^i C_o^m \qquad \text{Equation 17}$$

This ideal relationship generally applies to NAPL mixtures whose components are structurally similar. Broholm and Feenstra (1995) demonstrated near ideal behaviour for some chlorinated solvent VOCs. For structurally dissimilar alkane / aromatic mixtures, Leinonen and Mackay (1973) demonstrated the error in assuming Raoult's law was less than a factor of 2 as was also found by Cline et al. (1991) for fuels. Others have also reported that non-ideal departures may assume some significance (Garg and Rixey, 1999; Lesage and Brown, 1994). Nevertheless, the Raoult's law analogue may still be a valid first approximation in many cases and perhaps the only viable option where NAPL mixtures are complex and, or the composition is partly unknown. Although there are options available to account for non-ideal behaviour, for example universal functional activity coefficient (Broholm et al., 2005), the reality for most sites is that the uncertainties in variation in NAPL composition - that will not only vary spatially due to different sub-sources, but also temporally due to the preferential dissolution of the more soluble,

high mole fraction components (Eq. 8) - will override the uncertainties associated with non-ideal behaviour and most practitioners would rely upon the simplified Raoult's law analogue approach.

Much of the discussion of multi-component NAPL dissolution similarly applies to vapourisation. The effective vapour pressure of individual components within multi-component NAPLs is reduced due to the presence of the other components. If ideality is assumed the effective vapour pressure, P^i, of component *i* in the gas phase is given by Raoult's law (Fetter, 1999):

$$P^i = X_n^i P_o^i \qquad \text{Equation 18}$$

where P_o^i is the saturated vapour pressure of component *i* as a pure compound and X_n^i is the mole fraction. For mixtures of structurally similar VOCs, the ideal assumption reasonably holds and the above equation is reasonably valid from a practitioner's perspective. The vapourisation of simple mixtures (purely aromatic or aliphatic compounds) are well described (Wang et al., 2003), whilst the vapourisation and solubility of more complex non-ideal mixtures are not (Schaefer et al., 1998). Non-ideal mixtures require considerations of activities and, for example, may use the universal functional activity coefficient (UNIFAC) approach. The study by Broholm *et al.,* (2005) of the vapourisation of the Vaerlose airbase (Denmark) emplaced NAPL field source comprising 13 hydrocarbons observed vapourisation in accordance with Raoult's Law, with the exception of the aromatic compounds. These vapourised more quickly than the aliphatic constituents even though they were of similar volatility. Inclusion of UNIFAC predicted activity coefficients (calculated based on the functional groups present on the molecules) improved agreement with observed vapour concentrations.

4.5 SECONDARY SOURCE ZONES

Secondary source zones may develop over time that may become significant. The most well known example relevant to VOCs is their diffusion from NAPL sources present in fractures of dual-porosity aquifers to the adjoining matrix where substantial dissolved-phase or sorbed mass may accumulate in perhaps comparatively immobile matrix pore water (Parker et al., 1997). With time, NAPL present in the fractures, i.e. the primary source, may largely disappear and the matrix contamination then may serve as a secondary source as diffusion gradients are reversed to the now comparatively clean fracture zone. Reverse diffusion is much slower as the gradients are reduced and hence secondary source zones may contribute very long-term, low-level dissolved-phase contamination to mobile water migrating down through the fractures. The potential for this source condition should be recognised at old sources in dual porosity aquifers, particularly where NAPLs have been present. These aspects are considered further for Permo-triassic sandstone systems in Section 7.

4.6 DISSOLVED INORGANIC SALTS

Many waste disposal sites containing VOCs may also contain waste material that may generate significant concentrations of inorganic anions and cations in the leachate. Collectively the dissolved inorganic salts ion content is referred to as total dissolved solids (TDS). Leachate high in dissolved inorganic salts (which may be the case for many waste disposal scenarios) will effect the aqueous solubilities and activity coefficients of organic compounds and hence the dissolution of the VOC (NAPL) source. For neutral non-polar molecules, such as VOCs, it has been observed that for the predominant major ions found in water (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-), their increased presence leads to a decrease in aqueous solubility (due to an

increase in activity coefficient) (Schwarzenbach et al., 1993). This effect has long been recognised and is commonly referred to as “salting out”. The effect is related ions more tightly binding water into hydration shells, effectively reducing the volume of aqueous solution, so that this tightly bound water is no longer available for non-polar organic molecules to dissolve into.

Setschenow in 1889 established an empirical formula relating organic compound solubility in saline aqueous solutions ($C^{o}_{w\,salt}$) to solubility in pure water (C^{o}_{w}) (Schwarzenbach et al., 1993):

$$\log\left(\frac{C^{0}_{w}}{C^{0}_{w\,salt}}\right) = K^{S}[Salt] \qquad \text{Equation 19}$$

where [*Salt*] is the total molar salt concentration and K^{s} is the Setschenow or salting constant. The latter is a bulk constant relating the effectiveness of a particular salt (or salt combination) to salt out a given compound. The relationship for compounds such as benzene and naphthalene, compounds that reasonably span the VOC range, is valid over a wide range of salt concentrations (Gordon and Thorne, 1967). Although the value of K^{s} depends on both the salt and organic compound, the solubilities of most organic compounds (including VOCs) in sea water, where [*Salt*] is around 0.5 Molar, are lower by about 10 – 50 % compared to pure water (Schwarzenbach et al., 1993). The above relationship may be used to scale to salt concentrations at contaminated sites which for the most part would have a lower salinity than sea water. More polar compounds have a decreased salting-out effect as the polar group decreases the hydrophobic surface area and has a more favourable interaction with the ion present in the water; hence polar phenol would be less influenced than non-polar benzene.

Overall, the salting out effect is hence moderate, less than a factor of 2, but still may exert an important control in the long term dissolution of the source. A further impact of increased salt contents in the leached water is the increased density of the leached plume that may facilitate plume infiltration and density induced sinking in the saturated zone below (Simmons et al., 2002).

4.7 RELEVANCE

Knowledge of the various unsaturated zone source terms presented provides an important foundation upon which understanding of the nature of the dissolved-phase plume that may develop in the underlying unsaturated zone may be built. Estimations of VOC mass in a source zone and concentrations in dissolved-phase and vapour plumes may allow insights into the potential longevity of the source term and plume generation. In practice, however, there may be many unknowns concerning the source zones that practitioners may face including historical uncertainties such as the nature and timings of VOCs disposal, spatial complexities of the source zone and site investigation difficulties. These uncertainties need to be recognised in the assessment of dissolved plume infiltration through the unsaturated zone to underlying groundwater.

5 Plume transport and attenuation in the unsaturated zone

5.1 INTRODUCTION

Predicting the transport and attenuation of a dissolved-phase VOC plume percolating down through the unsaturated zone is a complex problem influenced by a variety of processes and site conditions. Following an overview of VOC transport and attenuation processes, transport of dissolved-phase and vapour plumes due to advection and dispersion / diffusion are considered as well as the exchange of VOC solute between these plumes often regarded as a single plume entity (particularly where their principal migration directions coincide). Attenuation due to sorption partitioning, biodegradation and abiotic chemical reactions that may reduce or prevent impacts to groundwater are assessed. Finally, the transport of VOCs across the capillary fringe and their incorporation into the underlying groundwater is discussed.

It is noteworthy at outset that the transport and attenuation of dissolved-phase VOC plumes through the unsaturated zone has only rarely been the direct focus of research or practitioner study. There are some studies as noted below. This does not reflect a lack of importance of the subject, however, but more likely the technical and practical challenges inherent to addressing the problems of VOC research undertaken in related areas including vapour plume transport, NAPL migration in the unsaturated zone and groundwater plume transport and attenuation. All these areas, however, do provide knowledge and understanding that can be transferred to the specific area being considered herein and hence their pertinent findings from a variety of field, lab and modelling studies are drawn into this review.

There are a number of important field-based or intermediate-scale large tank studies that have been conducted to examine VOC transport in the unsaturated zone that are listed in Table 1. These have all been conducted in shallow unconsolidated sand – gravel aquifer systems. The rationales given for study of each indicate none were directly focused upon assessing the percolation of a dissolved-phase VOC plume through the unsaturated zone. However, they do all address to some extent this problem, albeit tangentially and are appropriately referred to in the sections that follow. Studies in the literature that have most directly addressed the problem at hand, i.e. the infiltration of VOC-contaminated water from shallow source zones are modelling-based studies. Examples are the numerical modelling of Sleep and Sykes (1989) and the analytical modelling of Troldborg et al. (2009), with only the latter attempting to fit models to observed field data. Some well known contaminated sites in the US, for example the Picatinny Arsenal site (Smith et al., 1996), Savannah River site (Kirtland et al., 2003), Hanford site (Oostrom et al., 2007) and the Bemidji site (Molins et al., 2009) have been used for major research on the fate of VOCs in the unsaturated zone with the sophisticated numerical modelling work and conceptual models develop by Oostrom et al. on the Hanford site being particularly instructive. Some of these sites do, however, predominantly involve sources (e.g., LNAPL) located near the water table, for example the Bemidji site, but still provide relevant understanding. There have been field experiment studies where there has been controlled infiltration of VOC-contaminated aqueous phase. These have been restricted to dissolved-phase hydrocarbons (and not chlorinated aliphatic hydrocarbons, CAHs), for example, O'Leary et al. (1995) at the Borden site and Søvik et al. (2002) who undertook lysimeter trench experiments in the Gardermoen delta aquifer, Norway. Other major field site studies have provided detailed understanding of flow and contaminant transport in the unsaturated zone, but may not have specifically dealt with VOCs, for example, the Yukka Mountain site (Bodvarsson et al., 1999; Campbell et al., 2003).

Table 1 Examples of unsaturated zone field-scale or intermediate-scale large tank studies studies involving VOCs.

Location	Spill type	Source	Geology	UZ thick. (m)	Rationale for study	Reference
Borden site, Canada	Aqueous-phase infiltration	BTEX	Fine-medium sand	3-4	Experiment to observe attenuation of BTEX contaminated infiltration water	O'Leary et al., 1995.
Borden site, Canada	Emplaced DNAPL	TCE DNAPL	Fine-medium sand	3-4	Experiment to observe and model vapour migration; To evaluate groundwater contamination caused by vapour plumes.	Conant et al., 1996; Rivett, 1995.
Værløse Airbase, Denmark	Emplaced LNAPL	Jet fuel NAPL	Sand	3	Experiment to examine vapour transport and attenuation	Christophersen et al., 2005.
Practitioner case study sites, Denmark	Real spills	TCE DNAPL BTEX	Clayey till and sands	10	Practitioner case studies used to validate analytical models developed on leachable VOC models	Tuxen et al., 2006; Troldborg et al., 2009.
Gardermoen delta aquifer, Norway.	Aqueous-phase infiltration	T,X	Fine, coarse sands	3.5	Experiment to observe attenuation of BTEX contaminated infiltration water	Søvik et al., 2002.
Mediterranean Red Soil Volcani Center, Israel	Emplaced LNAPL	Kerosene LNAPL	Sandy loam	>1	Experiment to observe infiltration through a LNAPL source	Dror et al., 2001.
SCERES facility, France	Emplaced DNAPL	TCE DNAPL	Sand	12	Experiment to quantify DNAPL mass transfer flux to atmosphere and groundwater.	Jellali et al., 2003.
SCERES facility, France	Emplaced DNAPL	TCE/ PCE DNAPL	Sand	2	Experiment to assess transport in the UZ and capillary fringe for modelling validation.	Bohy et al., 2006.
LEAP tanks, Oregon, USA	Emplaced DNAPL	TCE	Sand; pea gravel	4.5	Experiments to assess density-driven vapour transport	Johnson et al., 1992.
Hanford site, Washington State, USA	DNAPL, wastewater releases	CT	Gravel, sand, silt and carbonate	Up to > 100	Assessment of DNAPL, vapour and dissolved-plume transport and remediation potential	Oostrom et al., 2007; Gee et al. 2007.
Savannah River site, South Carolina, USA.	DNAPL, wastewater releases	CT	sand, silty sand, thin clay	10	Assessment of transport, natural attenuation and remediation	Kirtland et al., 2003.
Picatinny Arsenal, New Jersey, USA	DNAPL, wastewater releases	TCE – waste ponds	Sand and gravel	2-4	Various, e.g., to determine if diffusion can explain fluxes through UZ	Smith et al., 1996.
Bemidji site, Minnesota, USA	Crude oil LNAPL releases	aliphatic, volatile aromatics: C_1–C_{35}	Glacial outwash	6	Assessment of Transport, MNA, e.g., biodegradation and geochemistry	Molins et al., in press.

5.2 OVERVIEW OF TRANSPORT AND ATTENUATION

5.2.1 Transport and attenuation processes

In order to provide context for the sections that follow, an overview of transport and attenuation processes that may influence the percolation of a leached VOC plume through the unsaturated zone is provided below.

Transport of VOCs down through the unsaturated zone is either by advection of dissolved-phase VOCs in the percolating water or diffusion / advection of VOCs in the air phase as a migrating VOC vapour. Both are subject to dispersion whereby for example more permeable geologic units may allow faster movement of VOC solute than less permeable units causing a dispersion of the dissolved-phase plume and vapour plume about their mean advective velocity. Both are also subject to diffusion that is much more important for the spread of vapours as gas-phase diffusion coefficients are c. 10,000 times aqueous-phase values. This will cause, for example, more radial diffusion of the vapour both laterally and to depth around the source zone and hence a spreading of VOC vapour contamination beyond the source zone footprint and the main dissolved-phase plume percolating downward beneath the source. The ready water / gas (Henry's law) partitioning that allows VOC exchange between the vapour and aqueous phases (in both directions) will however allow a secondary dissolved-phase plume to develop within and below the radially extending vapour plume as dissolution of vapour occurs into previously clean water percolating through that vapour.

The migration of vapour may also be influential in the transport of the dissolved-phase plume downward below the primary source. For slowly infiltrating dissolved-phase plumes, VOCs may undergo water / gas partitioning at the leading edge of (and within) the plume, particularly where concentration gradients are high, into the gas phase and effectively migrate in advance of the plume due to rapid gas-phase diffusion. The subsequent repartitioning back into the pore water ahead of the advecting plume effectively 'drags' the dissolved-phase plume downward. Likewise, when vapour concentrations are high there may be potential for density-induced vapour migration that may facilitate overall downward migration of the VOC plume. Volatilisation losses from the dissolved-phase plume may, however, potentially attenuate the plume if they occur laterally into areas where concentration and, or pressure gradients and hence diffusion and, or advection of the vapour is towards ground surface. As pressure gradients are temporally dynamic, due to climatic pressure variations and infiltration events etc., the direction of vapour advection may vary. Attenuation of the VOC plume may also occur due to sorption partitioning, abiotic chemical reaction or biodegradation. The latter two are regarded as more important as they may result in VOC mass loss, whereas sorption partitioning, unless irreversible (unlikely), will only retard the plume until all the available absorptive sites are occupied.

5.2.2 Current model simulation approaches

It is helpful to outline current model simulation approaches to the problem as they provide a convenient quantitative framework to the discussion of individual processes that follow. The recent work by Troldborg et al. (2009), for example, develops an analytical model approach that directly focuses on leached VOC plume migration in the unsaturated zone. The development of their analytical model is paraphrased below. Troldborg et al. give governing equations allowing for processes that are essential for representation of VOC leaching, namely: advection (in the water phase only in the direction of flow, i.e. vertical), dispersion, soil sorption from the water phase, Henrys law air – water partitioning, first order degradation in the water phase (due to biodegradation and/or chemical reaction). If linear, reversible and instantaneous equilibrium partitioning is assumed between phases and the Henrys law phase partitioning expression applies, then, the transport equations for water and air may be summed to give the following mass balance statement for the VOC contaminant that includes the solid, aqueous and gas phases (Troldborg et al., 2009):

$$\frac{\partial\left(R_w\,\phi_w + H\,\phi_g\right)C_w}{\partial t} = \nabla\left(\phi_w D_w + H\phi_g D_g\right)\nabla C_w - q_w\frac{\partial C_w}{\partial z} - \phi_w\lambda C_w \qquad \text{Equation 20}$$

where, R_w is the aqueous retardation coefficient, D_w is dispersion tensor in water, D_g is diffusion coefficient in gas (air), q_w is water infiltration rate and λ is a first order bulk degradation rate (other terms are previously defined).

Under the ideal partitioning and standard hydrophobic partitioning assumptions, the aqueous retardation coefficient R_w may be determined from (Bedient et al., 1997; Fetter, 1999):

$$R_w = 1 + \frac{\rho_b}{\phi_w}K_d = 1 + \frac{\rho_b}{\phi_w}K_{oc}f_{oc} \qquad \text{Equation 21}$$

assuming a linear isotherm for adsorption from water to solids,

$$K_d = K_{oc}f_{oc} \qquad \text{Equation 22}$$

Where ρ_b is the solid bulk density, f_{oc} is fraction of organic carbon, K_{oc} is the partitioning coefficient. The mass balance statement may be rewritten and further developed as follows (Troldborg et al., 2009):

$$\frac{\partial C_w}{\partial t} + v'\frac{\partial C_w}{\partial z} - \nabla D' C_w + \lambda' C_w = 0 \qquad \text{Equation 23}$$

where,

$$v' = q_w / R' \qquad \text{Equation 24}$$

$$D' = \begin{pmatrix} D'_x & 0 & 0 \\ 0 & D'_y & 0 \\ 0 & 0 & D'_z \end{pmatrix} \qquad \text{Equation 25}$$

$$\lambda' = \phi_w\lambda / R' \qquad \text{Equation 26}$$

$$R' = R_w\phi_w + H\phi_g \qquad \text{Equation 27}$$

The redefined retardation factor, R', hence incorporates the retarding effect of both sorption to the solid phase and partitioning to the gas phase and may be used to calculate the effective retarded velocity of the plume (v') by modification of the water infiltration rate by a factor of R'. It is noted that retarding due to partitioning to the gas phase will only occur when transport in the aqueous phase is faster than in the gas phase, which is rare. Also, partitioning will decline to zero as phase transfer reaches (Henry's law) equilibrium. Troldborg et al. (2009) proceed to define overall dispersion coefficients:

$$D'_x = D'_y = \left(\phi_w D_w^e + \phi_w \alpha_T v_w + \phi_g H\, D_g^e\right)/ R' \qquad \text{Equation 28}$$

$$D'_z = \left(\phi_w D_w^e + \phi_w \alpha_L v_w + \phi_g H\, D_g^e\right)/ R' \qquad \text{Equation 29}$$

Where α_L and α_T are the longitudinal (direction of vertical flow) and transverse dispersivities in the water phase respectively. Thus these coefficients include the contributions of air-water-soil phase-partitioning processes to the plume spreading process. Troldborg et al. (2009) modify slightly (recognising above definitions) the pore diffusion coefficients in the air and water phase of Moldrup et al. (2001) to give effective diffusion coefficients in the gas (D_g^e) and water (D_w^e) phases:

$$D_g^e = D_a^0 \frac{\phi_g^{1.5}}{\phi} \qquad \text{Equation 30}$$

$$D_w^e = 1.1\phi_w\left(\phi_w - 0.039 SA_{vol}^{0.52}\right)D_w^0 \qquad \text{Equation 31}$$

where D^0_a is the free air diffusion coefficient, D^0_w is the aqueous diffusion coefficient and SA_{VOL} is the porous media specific surface area. It is noted that alternative approaches to the above have been used by others to represent diffusivity and tortuosity, for example based on Millington - Quirk (e.g. Johnson and Ettinger 1991; Mendoza and McAlary, 1990; Thomson et al., 1997)).

The formulation hence extends analytical modelling of the scenario beyond that found in analytical-based commercial risk assessment leaching models, for example ConSim® (http://www.consim.co.uk/). Such models assume unsaturated zone advection plug flow of the dissolved-phase plume, dispersion just allowed for in the longitudinal (i.e. vertical) direction of flow, linear equilibrium sorption and a half-life allowing first-order decay of VOCs. Henry's Law volatilization losses from the plume are not considered, nor any transport of VOCs in the vapour phase. More flexibility for practitioner simulation of VOC leaching is, however, afforded by the US EPA code VLEACH that is a 1-D, finite difference model for making assessments of the effects on groundwater from the leaching of volatile, sorbed contaminants through the vadose zone (http://www.epa.gov/ada/csmos/models/vleach.html). It allows for liquid-phase advection, solid-phase sorption, vapour-phase diffusion, and three-phase equilibration as well as variation in soil properties, recharge rates, depth of water, or initial conditions. Modelling results in an overall, area-weighted assessment of ground-water impact.

Multiphase numerical models, however, that include NAPL, aqueous-phase, and air-phase migration and phase partitioning processes allow by far the greatest flexibility and representation of the complexity of VOC transport in the unsaturated zone of which dissolved-phase VOC plume percolation is one aspect. Most of these models have been used largely as research tools (e.g., Sleep and Sykes, 1989; Mendoza and Frind, 1990a,b; Mendoza and McAlary, 1990; Thomson et al., 1997; Karapanagioti et al., 2003; Jang and Aral, 2007; White et al., 2008), although some have examined transport at real sites (Oostrom et al., 2007). These models have the capacity to examine VOC dissolved-phase plume percolation through the unsaturated zone from a variety of source types, some of them have focused on transfer into infiltrating water and transfer to the water table via that process or vapour migration and contact (e.g. Sleep and Sykes, 1989; Mendoza and McAlary, 1990; Thomson et al., 1997; Jang and Aral, 2007). As indicated

earlier (Section 4.4), these models typically adopt a first-order mass-transfer relationships in NAPL dissolution, volatilisation and water / gas partitioning with equilibrium sorption partitioning between the water and solid phase. It is beyond the scope of this report to detail the numerical modelling approaches and formulations utilised and the reader is referred to the more recent works of Thomson et al. (1997) and Jang and Aral (2007) for such and also discussion of the improvements in model representation of flow and transport processes since the early 1990s.

5.3 DISSOLVED PLUME: ADVECTION AND DISPERSION

Advection is the bulk movement of dissolved-phase solute due to groundwater (water) flow. The mean position of the advective front is the mean position of the percolating water front in the unsaturated zone that may be estimated from infiltration or recharge estimates. Within the advecting VOC plume, dispersive solute spreading occurs due to mechanical dispersion arising from geological heterogeneity and pore-scale processes (e.g. friction) and diffusion. The latter is significant in low permeability horizons and dual-porosity matrices allowing VOC solute invasion. VOCs are, however, subject to additional partitioning or reactive processes per above and hence retardation and additional spreading of the plume front may occur. The overall dispersion coefficients (Equations 28, 29) defined by Troldborg et al. (2009) incorporate such VOC-based processes. To determine the actual longitudinal (α_L) (direction of vertical flow) and transverse (α_T) dispersivities (required by routine risk assessment models and within the formulation given by Troldborg et al.) would ideally require analysis of co-occurring conservative, non-reactive solute (e.g., chloride, bromide) released at similar initial times to the VOC.

The availability of such conservative data would be highly unusual causing dispersion estimates to be based upon other studies, typically recognising the scale dependence of dispersion and the heterogeneity of the geology present. In the saturated zone, α_L may typically be assumed to be around 10% of the travel distance based on groundwater tracer study datasets (Gelhar et al., 1992). In the unsaturated zone, however, travel distances are much smaller and also flow and transport are perpendicular to the predominant sub-horizontal layering. Furthermore, flow and transport are dynamic processes that vary in magnitude and direction due to the transient boundary conditions and variable water contents present not to mention fingering and fractures. Hence it becomes questionable if scale-based dispersion estimates from the groundwater literature may be translated to the unsaturated zone. For such reasons, Vanderborght and Vereecken (2007) reviewed and collated from the literature a database of 635 dispersivity values obtained from transport (leaching) experiments on soils and the underlying substrata. These data largely arise from the need to quantitatively assess leaching of nitrates and pesticides from soils and are derived from undisturbed soils cores and or columns and field assessments that are restricted in depth to a maximum depth of *c*. 2 m. Dispersion estimates over greater percolation distances hence largely require extrapolation from the findings at the < 2 m scale.

The field-scale estimates from Vanderborght and Vereecken (2007) are the most representative and over 0.8 – 2 m transport test intervals the median dispersivity was C. 0.07 m with 0 to 90% percentiles ranging from 0.02 – 0.2 m. The dataset was log normally distributed. The dataset allow the effect of the transport distance (d (cm)) on dispersivity (α_L (cm))to be examined with linear and power law relationships respectively developed by Vanderborght and Vereecken (2007):

$$\alpha_L = 0.046d + 1.23 \qquad \text{Equation 32}$$

$$\alpha_L = 0.33d^{0.62} \qquad \text{Equation 33}$$

Thus an increase in dispersivity with increase in travel distance was observed and in line with that found in groundwater tracer studies (Gelhar et al., 1992) and although the 10% rule of thumb used would have over-predicted the median estimates, but not substantially so and it may be roughly applicable to unsaturated zone soils. The limited transport scales studied (< 2 m) mean that prediction of unsaturated zone dispersion over larger length-scales is uncertain, of much interest to pollutant infiltration to a water table at moderate to substantial depths, both in rates of dispersivity increase and whether an asymptotic values is reached. Prediction of dispersion in the unsaturated zone is inevitably challenging due to the afore-discussed complexities of flow (Section 3). For example, dispersivity may also depend on flow rates and may perhaps decrease with increasing flow rates as the water-filled pore network becomes better connected and the tortuosity of the flow paths decreases. In coarse-textured soils, lateral redistribution of water and funnelling of water towards preferential flow regions may occur (Vanderborght and Vereecken, 2007). Geological layering (Pan et al., 2009) and bed-scale geological structure may exert a major control as illustrated by the significant sub-horizontal displacement of the bromide plume injected in the lysimeter trench experiments in the Gardermoen delta aquifer, Norway where tracer migration was observed to coincide with the direction of general geological dip (Søvik et al., 2002; Alfnes et al., 2004a) (Section 5.6.2).

We are unaware of any contaminated site, real or research, where conservative solute or injected tracer and VOC dissolved-phase data have been simultaneously collected from a leaching unsaturated zone source. VOC-based profiles collected in saturated or unsaturated zones have tended to focus on NAPL (Parker et al., 2002) or vapour occurrence and associate pore water contamination rarely (Smith et al., 1990, 1996), but not dissolved-phase plumes leaching from shallow source areas. Unsaturated zone solute profiles from the UK are fairly rare and if related to landfill sites tend to focus on inorganic major ions, for example chloride at the Burnt Stump landfill site on Nottinghamshire Triassic sandstone, but without comparable VOC data as many of the studies were conducted prior to the onset of the VOC groundwater issue becoming manifest (Lewin et al., 1992). Other profiles are typically nitrate profile data in the UK Cretaceous chalks and Permo-triassic sandstones unsaturated zones obtained largely by the BGS to assess agricultural impacts (summarised by Rivett et al., 2007). As unsaturated zone denitrification losses are usually very low, such profiles may be expected to yield some estimate of advection and perhaps dispersion in the unsaturated zone. In the US, for example, there has been significant work to assess flow and transport through the 600 – 700 m thick unsaturated zone at the Yukka Mountain site (potential repository for high-level nuclear waste) using, for example, conventional hydrological approaches, neutron logging and supporting porewater geochemical (total chloride, calcite, Sr, Cl^{36}), thermal data and some infiltration tracer (lithium bromide, sodium fluorescein) tests to examine water infiltration and transport (Bodvarsson and Tsang, 2003; Campbell et al., 2003; Liu et al., 2003; Bodvarsson et al., 1999). The predominant low geologic permeability of the site (unless within occasional fractured zones) means that parameter findings are most relevant to very low velocity sites with infiltration rates typically being just 2 – 20 mm / yr.

It is noteworthy that Troldborg et al. (2009) in their analytical modelling of shallow unsaturated zone leachable VOC sources based around VOC data from practitioner site studies indicate that the chosen water dispersivity values (based on Vanderborght and Vereecken, 2007) were deemed to be highly uncertain due to a lack of literature on the topic.

5.4 VAPOUR TRANSPORT

VOC vapour migration has an important influence on dissolved-phase plume migration due to the potential for VOC vapours to partition to pore waters that may be incorporated into the percolating dissolved-phase plume. In some scenarios, it is possible for vapour transport, rather than the slowly percolating dissolved-phase plume, to be largely responsible for VOC transport

to an underlying water table and the development of a groundwater plume (Baehr, 1987; Sleep and Sykes, 1989; Mendoza and McAlary, 1990; Rivett, 1995; Thomson et al., 1997; Jang and Aral, 2007). In other cases, vapour transport may result in significant losses of VOC to ground surface and atmosphere (Auer et al., 1996; Choi et al., 2002; Jellali et al., 2003). It is hence important to recognise the relative importance of vapour transport and interactions with the pore water as vapours may lead to either a reduction and delay (even substantial prevention through losses at ground surface), or else enhancement and early arrival, of VOC contamination at the water table (Sleep and Sykes, 1989). A wealth of VOC vapour-transport research has been conducted and an outline review is summarised below.

Vapour transport can be described by (Pankow and Cherry, 1996):

$$\frac{\partial}{\partial x_i}\left[\theta_a D_{ij}\frac{\partial c}{\partial x_j}\right]-\theta_a v_i\frac{\partial c}{\partial x_i}=\theta_a R_g\frac{\partial c}{\partial t} \qquad i, j = 1,2,3 \qquad \text{Equation 34}$$

where i and j represent coordinate directions, t is time, θ_a is the volumetric soil-gas content, R_g is the gas-phase retardation factor, c is concentration, v is velocity, x is distance and D is the dispersion coefficient:

$$D_{ij}=\alpha_T|v|\delta_{ij}+(\alpha_L-\alpha_T)\frac{v_i v_j}{|v|}+D_g^e\delta ij \qquad \text{i, j = 1, 2, 3} \qquad \text{Equation 35}$$

where α_L and α_T are the longitudinal and transverse dispersivities and D_e is the effective gaseous diffusion coefficient. Vapour-based transport away from a source zone may occur via both advection and diffusion discussed below.

5.4.1 Vapour Diffusion

Transport in the vapour phase is often dominated by diffusion because, diffusion coefficients for VOCs in the vapour phase are 4 to 5 orders of magnitude greater than those in the aqueous phase (Sleep and Sykes, 1989). This is especially where concentration gradients are highest , for example, near high-concentration sources, particularly NAPLs that may sustain gradients. This allows vapour plume migration in all directions radially from the source, although there may be plume direction bias due to advective pressure gradients, or other factors such as spatial water content distributions or geological heterogeneity.

Vapour diffusion is very sensitive to water contents, allowing most rapid vapour movement in drier unsaturated zones. At high water contents, the continuous air phase through geologic media becomes partly or fully discontinuous thereby decreasing the rate and extent of vapour migration as VOCs undergo dissolution (Henry's law partitioning) into the aqueous phase. Effective diffusion coefficients (D_g^e) in geologic materials varying in water content require consideration of the tortuosity that is estimated from various empirical relationships (Moldrup et al., 2001; Equation 30) such as that developed by Millington and Quirk (1961) that often underpins numerical model formulations (Mendoza and McAlary, 1990; Thomson et al., 1997; Jang and Aral, 2007):

$$D_g^e=D_a^0\frac{\phi_g^{7/3}}{\phi^2} \qquad \text{Equation 36}$$

This basic description has been extended to include information about the pore size distribution and intragranular pores within soil particles (Millington and Shearer, 1971). Moldrup et al. (2004), however, point to a lack of simple, predictive models that took into account different soil

types, but did not require knowledge of the entire soil-water retention curve. This was the impetus for their development of a three-porosity model that only used one measurement point on the soil-water retention curve. This model was validated by Kawamoto et al (2006) in their measurement of gas diffusivity on 22 different soils types ranging from sand to sandy clay loam, at a range of soil-water matric potentials.

The relationship between water saturation and the effective diffusion coefficient for TCE vapours has been investigated by Tillman and Weaver (2007). For a sandy loam, they observed at 10% water saturation the effective diffusion coefficient was *c*. 1.2×10^{-3} m^2/hr, whilst at 90% saturation, this decreased by three orders of magnitude to 1.3×10^{-6} m^2/hr. Such data and the relationships developed above illustrate the great sensitivity of VOC vapour diffusion to water contents. The significant spatial and temporal variation of water contents in the unsaturated zone and within and beneath a leaching, perhaps surcharged, source zone means that vapour diffusion coefficients and diffusive fluxes may be expected to exhibit orders of magnitude variation over quite limited spatial and temporal scales. The modelling study of Troldborg et al. (2009) concerning plume migration from a leachable VOC unsaturated zone source, likewise, illustrated high water contents reduced dispersion (diffusion) in the vapour phase and caused decreased horizontal spreading of the percolating plume.

The importance of vapour diffusion from NAPL sources has been shown in several field-scale or large tank-scale studies (Table 1). A sand-filled, subsurface experimental tank (SCERE's facility) involving a 5 litre TCE DNAPL source released into the unsaturated zone determined diffusion was the main transport process with the majority of TCE vapour (95%), corresponding to 3 g/m^2/d, being transported to the atmosphere (Jellali et al., 2003). A rapid rate of migration, largely attributed to diffusion, was also illustrated by Christophersen et al. (2005) at the Vaerlose airbase, Denmark where an emplaced unsaturated zone 10 litre NAPL source of thirteen different hydrocarbons exhibited radial migration to soil-gas probes within 20 m of the source in less than 1 day. The emplaced unsaturated zone NAPL TCE sources at the Borden site, Canada by Conant et al. (1996), likewise demonstrated that diffusion of VOCs in the gas phase was the dominant transport mechanism causing approximately radial development of the vapour plume over the *c*. 10 m radial zone monitored. Tuxen et al. (2006) and Troldborg et al (2009) describe a case study in Denmark concerning TCE that had leaked into a clayey till underlain by unsaturated sands where observed radial spreading away from the NAPL was ascribed to rapid vapour diffusion, estimated from model simulations to extend over 20 m a year after spillage although the gradients diminish over time, so growth eventually slows (Mendoza, 1995; Thomson et al., 1997; Jang and Aral, 2007). The aforementioned LEAP tank experiments showed both vapour-density driven and diffusion-based vapour transport (Johnson et al., 1992).

Atmospheric temperature variation at surface may alter shallow subsurface temperatures and influence rates of vapour migration. Enhanced vapour generation and migration was observed at the Borden site (Conant et al., 1996) and Vaerlose Airbase (Broholm et al., 2005; Christophersen et al., 2005) under high seasonal temperature (summer) conditions and attributed to increased vapour pressures, gas-phase diffusion coefficients and lower water contents. Non-uniform temperature-depth profiles caused variation in vapour concentrations of up to 15% over a temperature change of 2ºC for an experiment at the SCERE facility (Bohy *et al.,* 2006).

Vapour diffusion, along-side advection, is hence an important transport process that will cause VOC migration through the unsaturated zone and extend the area of pore water contamination that has potential to infiltrate towards the water table. For a small diameter high concentration source, e.g. a NAPL or effluent discharge point, lateral radial diffusion may significantly extend the effective source area footprint. For larger source footprints, say a leaching lagoon or waste tip, the radial vapour diffusion effect is proportionately less and potentially a diffusive 'halo' of vapour contamination may surround the facility to distances of 100 m or more for older sources (Oostrom et al., 2007). The importance of source area can be seen in the modelling of leachable VOC sources undertaken by Troldborg et al. (2009) who indicates that increased sizes of the

source area caused correspondingly reduced horizontal spreading of the percolating plume (including dissolved-phase and vapour phase components) such that a 1-D model could be used rather than a 3-D solution.

5.4.2 Vapour Advection

Advection in the gas phase occurs due to pressure or vapour-density gradients. Pressure gradients may cause preferential directional development of vapour plumes and may be driven by barometric pressure variations, vaporisation from the NAPL product, landfill gas generation, movement of water in the unsaturated zone, water table fluctuation, land-surface topography variation and wind, ventilated buildings - basements and the presence of more permeable pathways, either natural (e.g. a fissured horizon), or manmade (e.g. utility trenches or excavations) (Nilson and Lie, 1990; Nilson et al., 1991; Thibodeaux, 1981; Auer et al., 1996). Changes in water table elevation may cause advective gas flows and draw air into the unsaturated zone when water levels drop and vice versa when levels rise. The presence of ground surface covering may be relevant (Thomson et al., 1997). Where uncovered, pressure variation will be laterally uniform and if the unsaturated zone is thick with any low permeability layers, significant pressure gradients may develop. Where low permeability coverings are present, any cracks or discontinuities present may provide preferential conduits for vapour advection influenced by barometric pressure changes.

Auer et al. (1996) discuss the theory and model the influences of barometric pumping on VOC transport. Motion of air in the subsurface is induced by atmospheric pressure fluctuations that may vary cyclically due to diurnal temperature variation or episodic passage of high- and low-pressure fronts. With consideration of diffusive processes alone, then it is predicted that changes in the ambient atmospheric pressure will have marginal effect on VOC vapour transport as the air simply moves up and down and diffusion gradients do not vary. Auer et al. demonstrate that the induced motion will, however, lead to significant increases in the coefficient of mechanical dispersion (D) due to mechanical dispersion or velocity-dependent dispersion (Auer et al., 1996):

$$D = D_{mol} + \alpha|V| \qquad \text{Equation 37}$$

where α is the dispersivity and $|V|$ is a positive measure of the air velocity and D_{mol} the effective molecular diffusion coefficient. During barometric pumping, $|V|$ is not zero, even though the net velocity may be zero and hence $D > D_{mol}$. Pumping will then significantly influence VOC vapour transport rates, especially in high dispersivity, more heterogeneous geologies. The increased diffusion caused may lead to enhanced transport along the concentration gradient, which may be either towards ground surface from a deep source, or else for a partially penetrating plume, downwards, spreading contamination towards the water table. Auer et al. model the deep source scenario and indicate very significant VOC losses to atmosphere may occur compared to the diffusion-only case. It may represent a substantial passive loss mechanism, even in weakly heterogeneous systems - once mechanical dispersion is comparable to molecular diffusion, the pumping effect is significant. Pumping will also enhance surface losses as it rapidly mixes the gas near surface with the atmosphere allowing VOCs to escape more readily from that layer than by diffusion alone (Auer et al., 1996).

The relative importance of diffusive and advective flux losses to ground surface due to pressure and concentration gradients has been assessed in stratified and un-stratified drift deposits at the Picatinny Arsenal TCE-contaminated site, New Jersey (Choi et al., 2002). TCE gas-phase diffusive fluxes at the land surface were significantly greater than the advective fluxes unless near-surface high-moisture contents were present that caused a reduction in the diffusive flux that became more comparable to the advective flux. Diffusion was sensitive to surface air-filled porosity and moisture content changes (diffusive flux ranged from 1.74×10^{-3} to 1.7 mg m^{-2} h^{-1}

for air-filled porosities of 0.011 to 0.411 respectively), whereas advective fluxes were not highly sensitive to these factors (advective fluxes of 1.82×10^{-3} to 5.93×10^{-3} mg m^{-2} h^{-1} for similar air-filled porosities). Such VOC losses due to vapour migration to ground surface from shallow and deep unsaturated zone sources or even contaminated groundwater, represent an important means of reducing the potential for sustained development of groundwater plume, whether vapour losses occur via advective, and, or diffusive losses.

Vapour advection may also be induced by differential densities of concentrated VOC vapours near NAPL sources leading to vapour-density gradients and potentially a downward migration of a vapour plume to the water table (Schwille, 1988; Falta *et al.*., 1989; Sleep and Sykes, 1989; Mendoza and Frind, 1990a,b; Johnson et al., 1992; Altevogt et al., 2003; Jang and Aral, 2007). Density induced migration of vapours is an important issue for percolation of dissolved-phase plumes, as should dense vapour migration occur towards the water table, it may lead to contamination of clean pore waters ahead of the dissolved-phase plume and effectively extend the dissolved-phase plume contamination more rapidly to depth. This is most important where vapour densities are particularly elevated, for example in proximity to a volatile NAPL source and also where the geological strata are very permeable (Mendoza and Frind, 1990b; Sleep and Sykes, 1989). Numerical modelling sensitivity analysis by Mendoza and Frind (1990b) predicts for VOCs with high vapour pressures and molecular weights within high permeability environments (coarse sands or gravels), vapour-phase mass transported by density-dependent advection greatly exceeded that transported by diffusion alone. In their base case for a generic chlorinated solvent VOC, the hydraulic conductivity of 80 m/d used resulted in significant density-driven vapour flow, however, a reduction of an order of magnitude to 8 m/d showed advection no longer played a significant role and transport was dominated by diffusion. Likewise Mendoza and Frind (1990b) found that as the source strength and hence relative vapour density (RVD) declined, the importance of density driven advection also declined. The base case had a maximum RVD of 1.6 (24% molar fraction), but indicate by a RVD of 1.15 (c. 6% mole fraction) for the base case permeability produced only a weak advective influence due to the low pressure and density gradients. The RVD_i (of compound *i*)) may be calculated by (Johnson et al., 1992):

$$RVD_i = \frac{(P_i M_i + (1 - P_i) M_{air})}{M_{air}} \qquad \text{Equation 38}$$

where P_i is the vapour pressure and M_i the molecular mass of compound *i* and M_{air} is the molecular mass of air (c. 29g/mol). For saturated vapour pressures, the following RVDs may be calculated for instance: PCE 1.09; TCE 1.27; CT (carbon tetrachloride) 1.51; 1,1-DCE 2.54; and, Freon-22 3.0. Dilution of the VOC vapour pressure in air causes the density contrast to become progressively less with transport remote from a source.

The large-scale physical model experiments at the Oregon Graduate Institute LEAP tanks measuring 10 m × 9 m × 4.5 m deep illustrate at a controlled field scale the contrasts in behaviour for Freon-22 and TCE and a moist sand and a moist pea gravel with near surface emplaced sources (Johnson et al., 1992). The 100-fold greater permeability of the pea-gravel lead to a significant TCE density effect and migration to the underlying water table compared to the localised radial diffusion observed in the moist sand (Johnson et al., 1992). The observed vertical migration velocity due to density was over-predicted with the analytical expression of Falta et al. (1989) (although this may still be used to conveniently give an order of magnitude upper estimate), but was reliably modelled by the numerical model of Mendoza and Frind (1990a,b) that allowed for a combination of both diffusion and density-driven flow.

Sleep and Sykes (1989) likewise indicate the importance of density-driven flow in numerical modelling of a TCE DNAPL unsaturated zone source, as do Thomson et al. (1997) and Jang and Aral (2007) who specifically focus on this topic. Jang and Aral (2007) investigate density-driven

transport from an emplaced TCE NAPL source within a 8 m thick unsaturated zone, within a 200 m long × 16 m high domain. Comparison of their diffusion-only and density-driven advection (and dispersion) 1.0×10^{-10} m^2 permeability cases confirms density-driven gas flow with accelerated transport to the water table, but with diffusion becoming more dominant with distance from the source due to declining vapour density. Down groundwater gradient, development of both vapour / aqueous phase TCE was less than the diffusion-only case and attributed to density-induced advection causing increased outgoing gas flows that accelerated mass flow to ground surface laterally causing increased atmospheric losses. Nevertheless greater mass transfer rates were predicted from the source and into the groundwater in the density-driven case. Jang and Aral also examined the influence of soil permeabilities over the range 5×10^{-11} to 1×10^{-10} m^2. Reduced permeability causes decreased advection of gas and aqueous phases. All simulation cases exhibited density-induced advection with upstream contamination proving similar in all cases and ascribed to this process. For the lower permeability case, influence of greater gas flows and spread of contamination downstream was much reduced. Density-driven advection was the dominant process causing accelerated contamination of the saturated zone local to the source, but then groundwater flow, greater in the more permeable cases, became the key transport carrier allowing extended VOC migration downstream. VOC losses to atmosphere were fairly similar across the permeability range in contrast to the marked differences in transfers to groundwater that was most significant for the higher the permeability. As found by Thomson et al. (1997) (Section 5.5.1), the relative losses to atmosphere or accumulation in groundwater were sensitive to source location.

The USDOE's Hanford Site near Richland, Washington State, provides perhaps a very comprehensive evaluation of contaminant (Radiological, VOCs, etc.) within the unsaturated zone, likely one of the most detailed site investigations worldwide (Gee et al., 2007 and references therein). Some 580 m^3 of carbon tetrachloride (CT) are estimated to have been historically released to the subsurface. The site provides a primary example of the importance of vapour migration causing extensive contamination of the unsaturated zone and underlying groundwater in addition to direct entry of DNAPL to groundwater in parts of the site (Oostrom et al., 2007). This has been shown through both detailed site investigation and numerical modelling using STOMP model in the water-oil-air mode (WOA) that simulates migration of DNAPL, water and air phases, including density-driven flow (Oostrom et al., 2007; White et al., 2008). Oostrom et al. indicate the vapour plume is extensive because of enhanced gas phase advection caused by the density differences between the high RVD CT and ambient soil gas. The density differences caused CT vapours to move downward relatively fast, while a lower permeability Cold Creek unit and the saturated zone force the vapours to move laterally because of the reduced gas permeability due to higher water contents. The vapour plume was predicted to have spread *c*. 150 m in all directions and caused contamination of pore waters and underlying groundwaters well beyond the footprint of the DNAPL releases or infiltrating aqueous-phase discharges. The latter are indicated in the conceptual models of the site shown by Oostrom et al. in the form of wastewater disposal cribs, but were not the direct subject of Oostrom et al.'s paper. The saturated hydraulic conductivity values used by Oostrom et al. in the model (based on site data) generally ranged from c. 5-43 m/d with the low permeability Cold Creek silts that forced lateral migration being 0.1 m/d. The former range show reasonable agreement with the modelled ranges (8-80 m/d) predicted by Mendoza and Frind (1990b) (above) over which density-induced flow may be expected to become significant.

Hence for density-driven vapour flow to be important it requires elevated vapour concentrations to be present and thus a significant NAPL source in the unsaturated zone and also relatively permeable geologic formations, or discrete horizon to be present. When occurring they may be expected to allow density-driven vapour flow that may in turn lead to contamination of underlying pore waters and accelerated migration of VOCs to the water table. Vapour phase

contamination due to partitioning from dissolved-phase contamination alone in the absence of a NAPL source is unlikely to be sufficient to induce density-driven vapour flow.

5.5 PHASE PARTITIONING

VOCs plumes in the unsaturated zone may undergo phase partitioning via: water / gas partitioning processes that include water to gas partitioning and the reverse, gas to water (i.e. vapour dissolution) partitioning; and, sorption (and corresponding desorption) related processes. These include conventional sorption of VOC from water to the (geologic) solid phase under both water-saturated as well as sorption under partially water-saturated conditions that may include sorption partitioning directly from the gas phase to both the solid and the air-water interface. Such phase partitioning processes will modify the migration of advecting - diffusing VOC in either the (mobile or immobile) gas or water present and may lead to a chromatographic-like separation of VOCs that spend varying times in the mobile (usually gas) relative to semi-mobile (usually water) phases according to their VOC-specific partitioning potential. These phase-partitioning processes are considered in turn, recognising their mutual occurrence and influence means that complete segregation of discussion is not possible. The reasonable body of literature on VOC partitioning in the unsaturated zone has largely developed from the study of VOC vapour migration (Kim et al., 2005). This is not surprising as there are significant risks to groundwater and surface-based receptors associated with VOC vapour migration driving this research; and, it is difficult to sample the aqueous-phase reliably for VOCs at low water contents in the unsaturated zone (Saito et al., 2006; Smith et al., 1990; Smith et al., 1996) meaning that dissolved concentrations are back calculated from soil or gas-phase measurements. The literature is largely written from a vapour migration perspective typically associated with NAPL sources and generally necessitates some translation to the perspective of VOC plumes percolating down through the unsaturated zone from leached sources.

5.5.1 Water / gas partitioning

VOCs may undergo phase transfer between water and gas phases with gas / water partitioning or vapour dissolution into water causing transfer into the aqueous phase and the reverse process, water / gas partitioning, causing VOC transfer into the vapour phase. These may be referred to collectively as water / gas partitioning. At equilibrium, phase transfer rates decline to zero and the relative concentrations in the adjacent gas – water phases described by their temperature-dependent Henry's law constant, H (Equation 9). It is recognised too, that mass transfer across the phase boundary may be rate-limited and a first order mass transfer rate λ_H may be utilised to better describe VOC exchanges (Equation 11; Thomson et al., 1997). Such phase transfers are important and may exert, as shown by Thomson et al. (1997), significant control over whether a VOC is ultimately lost to the atmosphere at ground surface or else migrates to and accumulates in the underlying groundwater (Thomson et al., 1997; Troldborg et al., 2009). Radial spreading vapours may undergo dissolution of the vapour-phase VOC into porewaters and, where such water is infiltrating, potentially lead to accumulation of VOC in the underlying groundwater over a wide area (Mendoza and McAlary, 1990; Thomson et al., 1997; Jang and Aral, 2007).

The balance between ultimate atmospheric loss and incorporation in groundwater is also influenced by factors that are additional to, and also influential of, water / gas VOC exchanges; for example, infiltration rates and gas-phase advection, geologic heterogeneity and water contents. Various studies (Cho et al., 1993; Conant et al., 1996; Smith et al., 1996) indicate that retardation of VOC vapour plumes may occur due to vapour dissolution into semi-immobile pore water, they also indicate that elucidation of processes is challenging due the dependence of vapour advection, diffusion and retardation on vapour – water mass transfer rates, water contents and other complexities such as the influence of geological heterogeneity (i.e. grain-size and permeability distributions) on those processes and the greater retention of higher water contents in the finer-grained horizons. Such understanding is important for not just prediction of VOC accumulation in groundwater, but also modelling vapour migration from subsurface VOC

sources to buildings. Such models have developed from 1-D early formulations (Johnson and Ettinger, 1991) to now 3-D formulations (Abreu and Johnson, 2005) that may invoke the complexities of vapour transport within geological layers of varying permeability (Bozkurt et al., *in press*).

From a field perspective, there are several lines of evidence that indicate the importance of VOC vapour dissolution and water / gas partitioning. Cho et al. (1993) have shown VOC partitioning into percolating water during infiltration events and advection of dissolved-phase VOC mass downwards. Greater water contents (through surcharge of a lagoon or precipitation events) increase both water velocities and mass transport in the dissolved-phase whilst simultaneously decreasing vapour-phase diffusion. Smith et al. (1996) at the Picatinny Arsenal site, New Jersey, observed a storm event increase in water content from 17% to 22% over 3 hours leading to a diffusive TCE vapour flux decline from 0.2 to 0.06 μg m^{-2} h^{-1}. Vapour-phase TCE diffused into percolating water and was advected downwards. The importance of dissolution of radially diffused TCE vapours into infiltrating water surrounding the emplaced and covered TCE source of Conant et al. (1996) in the Borden site unsaturated zone was shown through the formation of shallow, laterally extensive, predominantly down-gradient (> 100 m) groundwater plume close to the water table interface (Rivett, 1995). The observed plume (although it has not been directly modelled) was not dissimilar from predictions made of soil-gas and groundwater contamination in the numerical modelling studies of Thomson et al. (1997) and Jang and Aral (2007). Some partly relevant field literature on water / gas partitioning may also be found in the studies on highly volatile tracers used to assess recharge through the unsaturated zone including CFCs and SF_6 (Cook and Solomon, 1995) and the soil-gas survey, largely practitioner, work directed to reconnaissance finding of VOC sources or plumes (Burston et al., 1993; Rivett, 1995; Thompson and Marrin, 1987). This literature is briefly referenced in Section 5.8 concerning VOC transfer across the capillary fringe (McCarthy and Johnson, 1993).

Not surprisingly from the above complications, modelling studies have provided the best insights into the importance of considering gas – water exchanges of VOCs. The modelling of Thomson et al. (1997), introduced in Section 4.4.4, is particularly instructive as they simulate cases with and without water / gas partitioning and with variable λ_H mass transfer rates. Without water / gas partitioning, infiltrating water can only become contaminated by flowing through the residual DNAPL source. The resultant steadystate dissolution and volatilisation rates were 10 g/d and 470 g/d, with the former comparing to some 288 g/d for the base case where partitioning was allowed. This illustrates that the dominant pathway for dissolved TCE in the base case was indirect through NAPL volatilising to form vapour that subsequently underwent gas / water partitioning, i.e., vapour dissolution into pore water. Water / gas partitioning exchanges (both directions) hence play an important role as most of the groundwater contamination observed in the base case was attributed to VOC partitioning from the gas phase into the infiltrating water phase. Without water / gas partitioning exchange, Thomson et al. demonstrate that as dissolved concentrations remain high at the source, the gradient driving NAPL dissolution is small and groundwater accumulation of VOC is less than in the base case. As Thomson et al. increased water / gas partitioning rate constants, they found decreased aqueous concentrations at the source that lead to increased dissolution rates, but decreased volatilisation rates due to higher gas-phase concentrations. The increased rates and higher vapour concentrations also caused slightly greater VOC accumulation in the underlying groundwater as there as increased VOC water / gas partitioning to infiltrating water occurred. Thomson et al. concluded that both the water phase and gas phase concentrations of VOC in the vicinity and down gradient of a residual NAPL source are most sensitive to the water / gas partition rate, λ_H, rather than volatilisation (λ_V) and dissolution (λ_D) rates. Thomson et al. (1997) also simulates the effects of infiltration rates, surface cover and seasonal (temperature, infiltration and cover) influences. Infiltration fluctuations are shown to be particularly important and the reader is referred to that work of Thomson et al.

The more simple formulations used in the analytical modelling of Troldborg et al. (2009) do not allow the same level of specific process insight that can be obtained through the more sophisticated and flexible numerical modelling approaches. Nevertheless, their modelling is illustrative of the importance of considering water / gas partitioning of VOCs in the leached scenario (amongst other factors). Their approach considered the pore water concentrations with distance leached from a shallow VOC source and determined that degradation and horizontal spreading were the most important attenuating mechanisms. Horizontal spreading simulated was principally ascribed to partitioning to and diffusion in the gas phase which caused a substantial decrease in contamination at the groundwater interface relative to vadose source zone pore-water concentrations. Over a depth of 18 m, the original source pore water concentration of 75 ug/l declined to below 2 ug/l at the water table due to the spreading process. The scenario was modelled with both a 1-D and a 3-D model, the latter of which is able to incorporate horizontal spreading. The mass being transported laterally in the vapour phase originated from the pore water and hence factors which increased the magnitude of horizontal spreading also decreased pore water concentrations. Besides source area sensitivity, the modelling was sensitive to degradation that could cause greater attenuation than horizontal spreading if degradation rates were high enough and also high water contents that reduced dispersion in the vapour phase causing decreased horizontal spreading.

The modelling of Troldborg et al. (2009) hence indicates the importance of collectively considering the processes that may control VOC transport and attenuation in the unsaturated zone and the importance of recognising the relative mobilities of VOCs in the vapour and dissolved phases and water / gas partitioning. The two case studies (practitioner data) simulated are illustrative of the complexities involved and the importance of the vapour phase on influencing dissolved plume transport. In one case study, pore water field profiles of BTEX contamination showed some resemblance to the modelled profiles, however, many sources of uncertainty preclude further comparison. Their other case study involved TCE that had leaked under an impermeable surface into 3 m of clayey till underlain by 7 m of unsaturated sands. Radial spreading away from the NAPL spill had been observed in the field (Tuxen et al., 2006). The model predicted that spreading by vapour diffusion was very fast and that after 1 year, TCE in the pore water at 25 m from the source had reached the drinking water limit (1 µg/l). The rapid spreading was caused by the volatile nature of TCE and the low water content in the unsaturated zone (0.1). This is in agreement with other numerical modelling studies that indicate rapid radial migration of vapours and associated contamination of pore waters and underlying groundwater (e.g. Mendoza and McAlary, 1990; Mendoza and Frind, 1990b; Mendoza 1995; Thomson et al., 1997; Jang and Aral, 2007).

Summarising, the transport of dissolved-phase VOC to the water table is shown to be largely due to vapour diffusion and gas / water phase partitioning to infiltrating or capillary held pore water. It also illustrates the importance of high concentration gradients facilitating vapour diffusion generated from the NAPL source. For lower concentration (non-NAPL) leachable source zones from which lower concentration dissolved-phase VOCs plume percolate through the unsaturated zone, the potential for phase partitioning to the vapour phase and hence roles of vapour diffusion are lower. Concentration gradients will be lower because less mass is present within the source and plume to sustain steep concentration gradients and mass partitioning to the vapour phase. Nevertheless if percolation rates are low (they often are below a capped lagoon) and also naturally with infiltration (or nitrate fronts) in UK major aquifers such as the chalk typically at 0.5 – 1 m / yr (Rivett et al., 2007), then partitioning of VOC to the vapour phase at the leading edge of the plume and vapour diffusion or advection downwards towards the water table and re-contamination of pore waters present may effectively accelerate the downward migration of the VOC plume to the water table.

5.5.2 Sorption with gas-phase partitioning

Sorption of dissolved-phase VOC plumes is a reversible phase-partitioning process that may retard the transport of a VOC plume. Sorption occurring in the unsaturated zone is distinct from that occurring in the saturated zone by virtue of the air phase and hence VOC vapours co-existing with the aqueous-phase plume. For soils that do not contain NAPL, four primary VOC phase-partitioning processes have been identified that may influence VOC vapour migration in unsaturated soils (Kim et al., 2001, 2005): (i) adsorption at the air–water interface, (ii) partitioning or dissolution into the bulk aqueous phase, (iii) sorption by the solid phase of the soil from the aqueous phase, and (iv) sorption at the solid surface from the gas phase. These phase partitioning, sorption-based, processes influence the bulk movement of vapour plumes or infiltrating dissolved-phase plumes through the unsaturated zone. The influence of each process depends upon the quantity, distribution and interactions of the various physical domains indicated above, the nature of the domains (e.g., type of organic-matter solid phase present) and the physiochemical properties of the VOC (Kim et al., 2005).

Much unsaturated zone research has been directed at understanding VOC sorption behaviour at low water contents to underpin assessment of vapour migration risks or performance or soil vapour extraction remediation (Chiou and Shoup, 1985; Pennell et al., 1992; Kim et al., 2005). Such research is relevant to predicting the percolation of dissolved-phase VOC plumes, both in its potential to indicate the fate of vapour-phase VOC associated with the infiltrating dissolved-phase plume and also in the discerning of higher water content thresholds at which process (iii) above, sorption by the solid phase of the soil from the aqueous phase, becomes the dominant process controlling sorption and converges to sorption behaviour found under water-saturated, saturated zone, conditions for which there has been numerous VOC-based studies (Allen King et al., 1996; Binger et al., 1999; Karapanagioti et al., 2001; Rivett and Allen-King, 2003) that provide supporting understanding.

Sorption and desorption are controlled by the amount and type of both minerals and various soil organic matter present. Mineral surfaces are primarily hydrophilic, whereas soil organic matter is primarily hydrophobic. Even at the very lowest water contents (i.e. arid conditions) that may be naturally encountered in the field unsaturated zone, it is still probable that water will largely, if not totally, cover the mineral surface. The experimental study by Kim et al. (2005), for example, indicates for their lowest volumetric water content (θ_w) studied of 0.021 (lower than that expected in the vast majority of field circumstances), the mean thickness of the water film formed on the soil surface was c. 4.0 nm that is equivalent to about 13 layers of water molecules. Experiments involving air-dried sediments exposed to air of varying relative humidity (RH), which is the partial pressure of water vapour normalised by its (temperature dependent) saturated vapour pressure) still indicate that at 100% RH water covers the majority of mineral surfaces (Goss, 1992). Steinberg et al. (1996) in their study of benzene and TCE sorption on a desert soil from the Nevada test site found that column effluents with RH values of 10 – 50% still yielded soil water contents of 0.5 – 2% (at 30^{o}C), calculated to be equivalent to slightly less than one monolayer of water to approximately four monolayers. Such low water contents are rare, except perhaps occurring near surface when very dry climate conditions arise, or else extremely arid environments exist, or else induced by a soil vapour extraction remediation scheme. The soil region overlying the water table could more typically contain moisture contents ranging from a few percent to near saturation with a typical field moisture content for the intermediate zone of a partially saturated soil layer being on the order of 10% unless porous media is fine grained and capillary retention much greater.

Unger et al. (1996) do, however, in their study of seven soils express some caution in relation to the above. Exposing dry soils to a RH of 100% led to variable relative saturation (RS) of pore water content varying from 0.02 – 0.2 and hence RH alone can be a poor indicator of the system saturation. Secondly, the majority of sorbent surface area resides in the intraparticle pores (pores less than 500 μm in diameter). As these pores are filled with water first, the majority of surface

area is water-covered at low relative saturations (RS). Unger et al. observed that for all their soils, greater than 80% of the surface area was water-covered at only 10% RS. Importantly, however, even at very high relative saturations (90% RS), all soils still had some fraction of the hydrated soil surface exposed directly to the vapour phase. It is important to note that these observations are based upon the wetting up of completely dry soils and hence primarily has implications for experiments conducted in that manner. Field soils are generally never expected to be completely dry, are exposed to repeated wetting and drying cycles and hence occurrences of soil surfaces directly exposed to vapours is likely much rarer in practice than encountered above.

Where water coverage of the mineral surface is present, i.e., the generally expected condition in the field, direct sorption of VOCs from the gas phase to polar mineral solids is unlikely (Ong & Lion, 1991; Goss and Schwarzenbach, 2002; Kim et al., 2005). It is then often and reasonably assumed as a first approximation that VOC sorption would primarily occur via process (ii), Henry's law partitioning or dissolution into the bulk aqueous phase, followed by process (iii), soil sorption from the aqueous phase that is expected, based on the wealth of water-saturated VOC sorption studies (Allen-King et al., 2002), to primarily comprise hydrophobic partitioning to the organic matter in accordance with the model originally proposed by Karickhoff et al., (1979) and widely used in water-saturated systems with Kd sorption coefficients typically estimated from the product of a measured soil f_{oc} and literature based K_{oc} (Equation 12) or else direct batch sorption measurements.

Research conducted on VOC vapour sorption at low water contents has, however, yielded significant insight that needs to be additionally considered. With decreasing RH, sorbed water is lost from the mineral surface that becomes increasingly available for VOC sorption directly from the gas phase. Many investigators (including Chiou and Shoup, 1985; Pennell et al., 1992; 1992; Goss and Schwarzenbach, 1998; Poulsen et al., 1998; Roth et al., 2002; Tekrony and Ahlert, 2001) have shown that VOC sorption is orders of magnitude greater under dry, less than c. 50 - 90% RH, conditions than wet conditions potentially only involving low percent contents of bulk water present. Significantly enhanced and increasing mineral sorption was found to occur with decreasing water (monolayer) coverage. The early work by Chiou and Shoup (1985) with various chlorinated benzene VOC vapours on dry Woodburn silt-rich soil indicated isotherms on oven-dried soils (0% RH) and at low RH (< *c*. 50%) were highly non-linear and sorbing with sorption capacities up to 2 orders of magnitude greater than those observed in water-saturated samples. Isotherms were of Brunauer Type II adsorption type and indicative of vapour condensation to form multilayer adsorbates. Direct vapour adsorption to the mineral phase (process (iv)) was the dominant sorption process at these low to moderate RH values and has been confirmed by many subsequent investigators (cited above). Chiou and Shoup's isotherms were near linear by 50 % RH with sorption magnitude continuing to decline that by 90% RH sorption becoming comparable to K_d data observed under water-saturated conditions.

Although the effect of water contents on the extent of VOC sorption in the presence of air phases had become well established by the early to mid 1990s, as noted by Pennell et al. (1992), the specific mechanisms controlling sorption of VOC vapours at RH values (or water contents) above which the sorbent is occupied by at least a monolayer of water remained unclear and provided the impetus for continued research. That work largely focused upon assessing the actual contributions of the phase partitioning processes (i) – (iv) listed above. Additionally Unger et al. (1996) indicated that vapour condensation in micropores may be a further process. The study by Unger et al. (1996) examining the relative importance of these contributions for 7 soils and several VOCs (benzene, toluene, TCA and TCE) with water contents ranging from oven-dried to full 100% relative saturation (RS) of pore space provides a comprehensive experimental dataset showing expected strong non-linearity and high sorption at 0% RS and more linear and much lower sorption at higher RS values. The data are well fitted by BET isotherms. Unger et al. note sorption decreased most significantly within the RS range of 0.0-10% and attribute this to the intraparticle pores (<500 Å diameter) being filled with water, and

hence it is the range of RS where most of the soil surface area is being covered by water and direct vapour sorption to solids is progressively less.

The role of process (i), adsorption at the air–water interface was indicated to be important by Pennell et al. (1992) based on observed data and predictions based on the Gibbs equation. Unger et al. (1996) recommended it as a preferred future approach, but were unable to assess its contribution. It was not until the advent of the interfacial tracer techniques (Brusseau et al., 1997; Kim et al., 1999) that specific air-water interfacial areas and hence contribution to sorption by this process could be estimated. The vapour-based work by, for example, Silva et al. (2002), Roon et al., 2005 and Kim et al. (2001, 2005) explored this process in detail. Kim et al. (2005), for example, aimed to quantify the various phase partitioning processes (i) – (iv) contributing to retardation of a VOC as a function of water contents that in their experimental work with TCA and PCE range over field-relevant θ_w values of 0.02 to 0.24 for a total soil (sandy silt) porosity θ of 0.44 (i.e. saturations of water, S_w, 0.05 -0 .55).

Various composite retardation factors have been proposed that allow estimation of VOC retardation due to the component phase partitioning processes (e.g., Kim et al., 2005; Silva et al., 2002). Kim et al. reasonably assumed based on the literature and their experimental observations (and above discussion) that direct sorption of VOCs from the gas phase to solid surfaces is unlikely when soils contain bulk waters (vast majority of field conditions) and hence sorption process (iv) is disregarded in their analysis. They further assumed that a total retardation factor (R_t) may be defined based on linear additivity of effect of each phase partitioning process (Brusseau et al., 2005) and can be expressed as (Kim et al., 2005):

$$R_t = \beta_g + \beta_w + \beta_i + \beta_d \qquad \text{Equation 39}$$

where β represents the partial retardation factor with the subscripts g, w, i, and d referring to VOC retention in the gas phase, in the aqueous phase, at the air–water interface, and sorbed at the solid domain of the soil from aqueous phase, respectively. β_g takes the value unity and the other β values are defined by standard local equilibrium partitioning expressions, with β_i related to a_i is the specific air–water interfacial area and K_i the interfacial adsorption coefficient (Kim et al., 2005). The laboratory observations and model simulations of Kim et al. (2005) for TCA (K_{oc} 364 cm^3/g) a weakly hydrophobic VOC (comparable to TCE) and PCE (K_{oc} 846 cm^3/g) a quite hydrophobic VOC are instructive and shown in Figure 6 that plots variation of R_t and component β values as a function of water content.

The reader is referred to Kim et al. (2005) for the full data discussion that importantly provides quantified insight into the component partitioning processes controlling the retardation of the VOCs under varying water content conditions. β_w values were expected and observed to be similar for TCA and PCE as their Henry's partition constants were similar. Likewise, their air-water interfacial adsorption coefficients and a_i values were similar and hence their β_i values were also comparable. Hence, the difference in R_t values in this instance was primarily ascribed to the difference in β_d values and hence K_d values reflecting the different extents of sorption of TCA and PCE from the aqueous phase by the soil, i.e., process (iii) as a consequence of their differing hydrophobicities. All three retention processes contributed equally to R_t for TCA at higher water contents, however, at reducing water contents interfacial adsorption (β_i) was dominant by a θ_w of 0.17 values and very dominant at low water contents as it increased with increase in a_i with corresponding (<20%) sorption to soils from the aqueous phase.

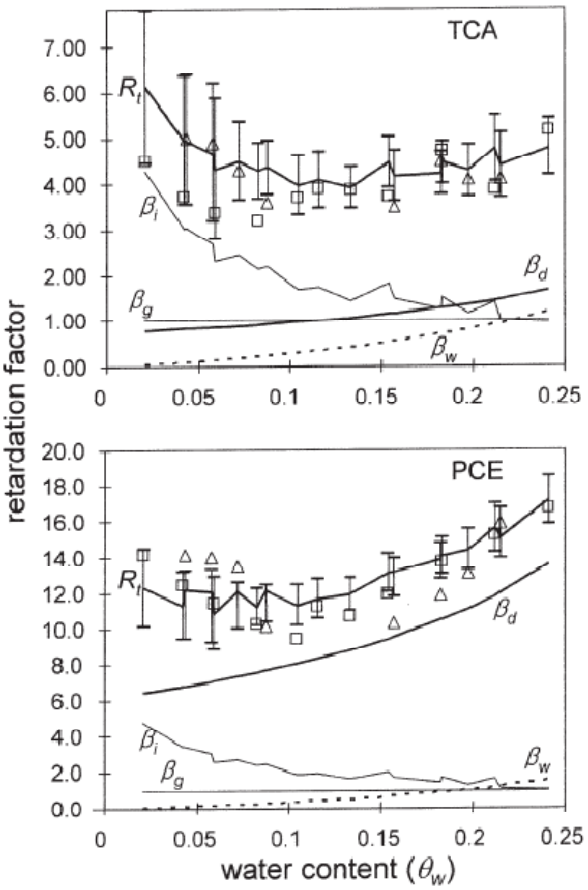

Figure 5. Data from Kim et al. (2005) showing retardation factors for PCE and TCA as a function of water content.

The rectangles (first replication) and triangles (second replication) represent measured total retardation factor (Rt) values; solid lines represent predicted total (Rt) and partial (β) retardation factors where βg, βw, βi, and βd referring to VOC retention in the gas phase, aqueous phase, at the air–water interface, and sorbed at the solid domain of the soil from aqueous phase respectively.

Sorption on to the dry soil is not reported, however, by way of comparison previous experiments by Kim et al. (2001) on a Dover AFB loamy sand indicated that TCA sorption was an order of magnitude greater reporting an R_t value of 524. In contrast the more hydrophobic PCE, exhibited R_t values for which β_d was dominant throughout with interfacial adsorption only becoming comparable by a θ_w of 0.02. For both TCA and PCE, the comparability of the predicted and observed R_t values indicates the local equilibrium assumption for the partitioning processes was reasonably valid under the experimental conditions.

In summary, the sorption of VOCs in the presence of air under partially water-saturated conditions is very sensitive to water contents. For rigorous treatment, a multi-mechanistic approach is required. For water contents typically anticipated in the field it is necessary to consider partitioning processes (i) adsorption at the air–water interface, (ii) partitioning or dissolution into the bulk aqueous phase, (iii) sorption by the solid phase of the soil from the aqueous phase. The relative importance of these retention processes will depend on the VOCs partition coefficients (K_d, K_i, K_H) and the availability of sorption sites of the soil characterised by ρ_b, a_i and θ_w. Notably, recent work indicates air-water interfacial adsorption may assume significant importance at low to moderate water contents approaching θ_w of *c*. 0.2 and possibly more depending on the VOC and soil nature. At very low water contents, essentially near dry conditions that are assessed through experiments on dry soils with air at sub-saturation humidities, where RH values are less than c. 50-90%, partitioning process (iv) sorption at the solid surface from the gas phase becomes dominant. It may lead to VOC sorption on dry mineral

surface that is 2 – 4 orders of magnitude greater than that observed under water-saturated conditions, however, such conditions are generally very unlikely to occur in the field. Although some of the earlier research suggested there may be convergence to water-saturated sorption behaviour at very low water contents, more recent work discussed above suggests this may or may not be the case due to the contribution of air-water interfacial adsorption. Nevertheless for more hydrophobic VOCs and greater sorbing soils (i.e. high f_{oc} soils), solid phase sorption from the aqueous phase may become dominant at relatively low water contents and become increasingly dominant for all VOCs at moderate to high water contents. Models under those conditions that assume simple K_H vapour-phase to aqueous-phase partitioning and K_d, sorption by the solid phase from the aqueous phase (Troldborg et al., 2009) would then be expected to be reasonably valid.

5.5.3 Sorption under water-saturated conditions

Sorption studies conducted under water-saturated conditions aimed primarily at groundwater assessment are primarily useful in two areas with respect to unsaturated zone sorption assessment. Firstly in the provision of K_d data and secondly in the consideration of non-ideal sorption processes. These areas are considered briefly below.

K_d data

Simple K_d data may be used to parameterise VOC partitioning between the aqueous-phase and solid phase. It has been indicated above that under many partially saturated water content conditions, K_d partitioning is an important contributory process to VOC retardation at both relatively low water contents as well as high water contents where it is increasingly dominant and the only sorptive partitioning process operative under fully water-saturated conditions. The latter conditions may occur under infiltration events or be permanently present in for example dual-porosity aquifers with a small-pore rock matrix (e.g. chalk) where diffusive migration of contaminant in fractures will be retarded by sorption that reliably characterised by water-saturated K_d data. Such K_d data would be used in the partitioning formulations given earlier between phases in the source zone (Equation 12), the unsaturated zone dissolved-phase plume migration formulation given by Troldborg et al. (2009) (Equation 27) and within typical practitioner risk assessment leaching models.

Literature estimates of K_d and K_{oc} (back calculated from Equation 21 where lab studies have measured both K_d and f_{oc}) for VOCs are fairly plentiful, in the literature, particularly for PCE, for example, that is regarded as a "model" VOC to study (US EPA, 1996). VOCs range form being quite hydrophilic with solubilities as high as 20,000 mg/l for dichloromethane to weakly hydrophobic with for example PCE having a solubility *c*. 100 fold lower. Some of the more soluble (and sometimes volatile) VOCs are very weakly sorbing. It may be challenging to measure their sorption coefficients in low f_{oc} soils and retardation may be fairly minimal. For example, in the Borden aquifer (Canada) of low f_{oc} c. 0.02% a dissolved TCM plume was observed to be near conservative (R = 1) and TCE minimally retarded at R ~1.2 (Rivett and Allen King, 2003; Rivett et al., 2001). Where VOC solubilities exceed *c*. 1000 mg/l (i.e. TCE) and solid-phase f_{oc} contents are low, then retardation may be fairly minimal approaching conservative behaviour. More sorbing VOCs, typically of lower volatility, show low to moderate sorption. For example, PCE at the Borden site has been found to exhibit retardation factors in the *c*. 1.5 to 5 range with variation ascribed to non-ideal sorption influences (Rivett and Allen King, 2003). For example, a mean water infiltration time of water to the water table of say 10 years would lead to mean arrival times of a PCE plume ranging from 15 to 50 years based on reliance of single value extremes for those data.

Non-ideal sorption

Due to the inherent complexity arising from the presence of air, it becomes challenging to also study other non-ideal sorption processes in partially saturated samples, such as kinetic rate-limited sorption, linearity of sorption under high water contents and competitive multi-solute

sorption, so knowledge is often extrapolated from the water-saturated non-ideal sorption research literature. Although widely studied (Hohener et al., 2003; Xia and Ball, 2000; Allen-King et al., 1996, 2002), non-ideal sorption is not routinely incorporated into risk assessments due to the complexity of the mathematical formulations or the challenge of obtaining relevant data. The non-ideal sorption processes discussed are generally unlikely to have been considered in much detail, if any, at the vast majority of real sites. Although a challenge to quantify, practitioners should be aware of their potential influence on transport in the unsaturated zone and, where potentially important, provide some quantification lab batch or column experiments. A brief consideration of some non-ideal sorption processes is made below.

Non-linear sorption and organic matter type

Sorption isotherms may exhibit non-linear sorption with concentration (that reflect different energy sorption sites) under water-saturated conditions; however, these are typically mildly non-linear and often parameterised by an empirical Freundlich partition coefficient (K_f) and non-linearity exponent as in the following relationship:

$$C_s = K_f \left(C_i'\right)^{1/n} \qquad \text{Equation 40}$$

Where C_s is concentration in solid phase, Ci is equilibrium concentration and n is a constant. The retardation (due to sorption) of an advancing plume front of solute i is (Crittenden et al., 1986):

$$R_i = 1 + \left(\frac{\rho_b}{\phi}\right) K_{f_i} C_i^{[(1/n_i)-1]} \qquad \text{Equation 41}$$

where ρ_b and ϕ are the bulk density and porosity, respectively. Where large ranges in dissolved concentration exist such as where sporadic NAPL sources exist near cleaner source zones or concentrations have become dispersed through vapour migration and long residence times in the unsaturated zone, non-linearity may result in significant differences in retardation factors within a plume. Typically, the non-linearity exponent is <1 and enhanced retardation occurs at lower plume concentrations whilst the higher concentration core of the plume moves faster resulting in an overall compression of the plume front. Rivett and Allen-King (2003) illustrate that the influence of mild nonlinearity (1/n of 0.91) on TCE and PCE at the Borden site is significant with calculated retardation factors doubling over the concentration studies. The challenge for most sites would be obtaining reliable non-linearity terms as high quality lab work is required to confidently determine such indices particularly where non-linearity is mild.

Non-linearity may in part be attributed to the differing nature (or types) of the organic matter sorbing phase (i.e., the f_{oc}) that may lead to differing sorption capacities (Grathwohl, 1990; Rutherford et al., 1992; Allen-King et al., 2002). This may likewise explain literature variation in K_{oc} seen for individual compounds and lead to some errors and, or uncertainty in simple calculations of K_d based on Equation 12. Two types of organic carbon sorbent have been suggested (Weber et al., 1992): a soft carbon or amorphous phase such as humic matter; and, a hard carbon, or relatively condensed organic matter phase such as kerogen (also referred to as labile and non-labile organic matter by others). Kleineidam *et al.* (1999) reported isotherm linearity for a number of different organic matter types. The most mature and altered organic matter, incorporating plant remains, charcoal and coal particles were found to have the most non-linear isotherms (1/n of 0.4-0.5) and highest sorption magnitudes, whilst the organic matter facies containing more modern, unaltered particles such as organic matter sorbed to grains (humic and fulvic acids) were observed to have near-linear sorption isotherms (1/n of 0.9-1) and exhibit lower magnitude sorption (Accardi-Dey and Gschwend, 2002; Binger et al., 1999; Chiou et al., 2000; Karapanagioti et al., 2001). The type of organic matter may also have kinetic implications with rate-limited sorption / desorption much more significant in the non-labile fractions (Allen-King et al., 2002). There is a lack of data concerning the organic carbon content of unsaturated compared to saturated zone materials, but differences may be anticipated to arise

that reflect the varying age and nature of their deposition environments, or perhaps modern influences arising from anthropogenic inputs or natural inputs, for example biomass.

Competitive sorption

When multiple VOCs or other organic contaminants are present, there is the potential for 'competitive sorption' to occur where the various contaminants compete for sorption sites (Broholm et al., 1999). This is highly probable for many partially penetrating unsaturated zone sources as most will have received a mixture of wastes. The Ideal Adsorbed Solution Theory (IAST) has been used in various environmental engineering applications to describe competitive sorption processes, including dissolved VOCs in porous media (McGinley et al., 1996; Rivett and Allen King, 2003). Rivett & Allen-King (2003) demonstrate reduction in PCE sorption in the presence of dissolved-phase TCE in batch experiments on Borden sand and invoke both competitive sorption and non-linearity to explain in part the marked reduction in retardation in high concentration plumes observed from a DNAPL source compared to dilute concentration plume injection experiments at Borden (MacKay et al., 1986). They also argue these non-ideal processes have influenced the relative retardation of PCE, dichlorobenzene and carbon tetrachloride VOCs in the dilute plume. The competitive sorption of PCE and TCE has also been considered by Li and Werth (2001) who indicate the competition is primarily ascribed to the amount of hard organic carbon present.

Rate-limited sorption

Kinetic rate-limited (non-equilibrium) non-instantaneous sorption may be expected to be most significant where percolation velocities are highest and there is insufficient time for the migrating dissolved-phase to attain equilibrium partitioning with the solid phase. Storm-event infiltration, soakaways, particularly leaky lagoons and rapid flow through fractures offer potential for such kinetic effects that would lead to a non-assymetric VOC breakthrough concentration profile at the water table with an earlier arrival time compared to that predicted by simply dispersion and ideal sorption. Many workers have shown that chemical non-equilibrium due to slow diffusion-based sorptive partitioning may cause kinetic sorption effects for VOCs, even in weakly sorbing low f_{oc} sands (Ball and Roberts, 1991; Thorbjarnarson and Mackay, 1994). Kinetic, rate-limited sorption, although probable in the unsaturated zone, would be challenging to demonstrate amid the influences of other processes, for example volatilisation. Some unsaturated zone research has, however, been conducted on pesticide leaching through soil macropores with similar arrival times of sorbing and non-sorbing tracers occurring and ascribed to rate-limited sorption (Scotter, 1978). Malone et al. (2004) also found preferential flow resulted in breakthrough of the herbicides glyphosphate and glufosinate that was independent of their sorption properties. Most pesticide work is focused in the shallow source zone where Jarvis (2007) summarises non-equilibrium transport is controlled by soil horizon morphology (size distribution of preferential flow paths, aggregate skins, grade of aggregate) and basic soil properties (texture, organic carbon content). It is important to note that rate limited sorption not only impacts the leading front of a percolating plume, but also the tailing release from a largely depleted source. Diffusion-based rate-limited sorption causes reverse desorption to be hysteretic relative to forward sorption as the intra-sorbent diffusion gradients will differ. Gradients will be reduced in the reverse desorption phase and may lead to prolonged slow-release and tailing of a plume (Ball and Roberts, 1991; Zhang and Brusseau, 1999; Shih 2007). Sorption diffusivities may be an order of magnitude lower during desorption from organic matter as shown for TCE by Shih (2007) (1.1×10^{-8} cm^2/s compared to 3.0×0^{-9} cm^2/s) with similarly prolonged desorption found by Kommalapati et al. (2002) studying hysteretic sorption - desorption of hexachlorobutadiene on clayey soil from a Superfund site in North Baton Rouge in Louisiana. Prolonged tailing, or "bleeding", of VOC from a contaminated unsaturated zone may hence be anticipated where rate-limited sorption is significant.

5.6 BIODEGRADATION

Biodegradation resulting in compound breakdown to simpler daughter products may occur within unsaturated zone pore waters as long as suitable bacteria, carbon sources, terminal electron acceptors and other nutrients are present and environmental factors such as pH and temperature are conducive. Oxic conditions of the unsaturated zone typically cause aerobic processes to be dominant, however, niche anaerobic zones may develop during times of high water saturation and organic loading and oxygen is readily consumed. Much VOC biodegradation research has been undertaken in the saturated zone driven by monitored natural attenuation (MNA) interests, both in petroleum hydrocarbons and chlorinated aliphatic hydrocarbons (CAHs) (Rivett and Thornton, 2008; Weidemeier et al., 1999). Relatively limited research is available for the unsaturated zone, particularly for the CAHs. Review of the hydrocarbon and CAH biodegradation literature follow an introductory section on bacterial activity distribution in the unsaturated zone, largely drawn from the agricultural chemical (nitrate, pesticide) literature (Pothuluri et al., 1990; Ajwa et al., 1998; Rivett et al., 2007). The more rural nature of those studies needs to be considered in transfer of understanding to industrial VOC sites where important soil horizons may be lacking.

5.6.1 Distribution of bacterial activity

Most bacterial resources in the soil are plant derived and degraded rapidly causing concentrations of natural substrates for bacteria to decrease rapidly with depth. The underlying unsaturated zone is hence typically less microbially active with lower carbon and nutrient fluxes (Beloin et al., 1988). For example, bacterial activity / biomass at the Purdue University Agronomy site was greatest near surface and in the saturated zone allowing rapid biodegradation of glucose and phenol compared to rates in till at mid-depths in the unsaturated zone (Konopka and Turco, 1991). Biomass with depth may relate to the distribution of compounds essential to biomass growth. Carbon distribution with depth has been variously modelled as a power function (Bennema, 1974) and more complex exponential functions (Bernoux et al., 1998; Jobbagy and Jackson, 2000).

Nutrient concentrations may be modelled similarly and are influenced by clay content, organic matter (controlling availability of exchangeable ions) and dissolved organic nutrient abundance. Decreasing clay content and organic matter with depth may influence nutrient supply (Konopka and Turco, 1991). Low water contents were observed by Keift et al (1993) to limit the availability of carbon causing microbial culture counts to increasse by 200 fold when water contents increased (Hickman and Novak, 1989). Microbial activity, as expressed by dehydrogenase activity (Taylor et al., 2002), N mineralization (Ajwa et al., 1998), enzyme activity (Taylor et al., 2002) and incorporation of $^{32}PO_4$ (Konopka and Turco, 1991), have been observed to decrease with depth and may be ascribed to declines in microbial abundance and substrate availability (Swensen and Bakken, 1998). Filtering of bacteria, typically of micron or greater size, may occur in geological deposits of small pore size and may lead to a straining of bacteria (Gaganis, et al., 2004), With addition of the required nutrients, respiration rates can, however, compare to those near surface (Chapatwala et al., 1996; Dick et al., 2000). At polluted sites, increases in bacterial populations and major changes in the local biogeochemical conditions may also be driven by the pollutant itself where it is the substrate, e.g. hydrocarbons (Molins et al., in press).

5.6.2 Biodegradation of hydrocarbons

Bacteria extract energy from organic compounds during catabolic reactions as a result of oxidation processes (Vogel et al., 1987). Electrons from the oxidised chemical (electron donor) are transferred to an electron acceptors resulting in its reduction. Greatest efficiencies and energy returns for the bacteria occur with oxygen acting as electron donor under aerobic conditions. Biodegradation is typically assumed to occur on contaminant partitioned into the water film surrounding soil. Air in contact with water films will provide a steady supply of dissolved

oxygen (DO) expected to approach saturation at *c*. 10 mg/l (temperature dependant) unless the composition of the air markedly changes due to for example biodegradation processes leading to enriched carbon dioxide or methane and may lead to extensive or more localised anaerobic niche environments. VOC biodegradation studies of the unsaturated zone have generally involved aromatic hydrocarbons or occasionally chlorinated alkane/alkenes.

There have been a few studies examining biodegradation occurring during the infiltration of dissolved-phase aromatic hydrocarbon VOCs. O'Leary et al. (1995) investigated the feasibility of surface application and natural attenuation in the unsaturated zone for remediating BTEX under field conditions at the Borden site, Canada. A surface area of 25 m^2 underlain by *c*. 3.5 m of unsaturated sands soil was continuously drip irrigated for periods of > 9 days at 43 and 72 cm/d with water containing BTEX at 8 and 11 mg/L. Nitrogen was added to the soil as a nutrient for the final third of the investigation. Before reaching the water table, BTEX mass losses prior to reaching the water table were from 65 to ~100% with only 6% mass losses attributed to volatilization from the soil. Most loses were due biodegradation, mainly in the top 50 cm of the soil, where more inorganic nitrogen and organic carbon were present. Biodegradation rates increased with applied concentration, nitrogen addition, i.e. a limiting nutrient, and exposure to BTEX. To meet drinking water standards for benzene (5 µg/l) in the underlying groundwater, it was necessary to apply nitrogen. Under those conditions the test plot could treat 18 m^3/d of water containing BTEX concentrations of about 11 mg/l to drinking water standards. Zero order degradation rates were calculated ranging from benzene at 14.0-20.5 mg $(kg\ d)^{-1}$ to xylene at 1.3 1.9 mg $(kg\ d)^{-1}$.

Allen-King et al. (1994, 1996b,c) conducted parallel laboratory column experiments to O'Leary et al. (1995) infiltrating dissolved-phase toluene in a c. 2 m long unsaturated zone Borden sand column. Trichloromethane (TCM, *aka*. chloroform) was used as a volatile, marginally sorptive, and recalcitrant tracer so that mass loss for the degradable compounds in the column could be confidently attributed to transformation. At < 4 mg/l, TCM did not affect the rate of toluene oxidation and TCM itself was not transformed aerobically. Transformation rates under N-limited conditions but sufficient oxygen were 8 - 35 mg $(kg\ d)^{-1}$ and appeared to follow zero order kinetics. Toluene-degrading microoganisms increased significantly in activity and numbers with exposure to toluene. Low CO_2 production to oxygen consumption ratios suggesting incomplete toluene mineralization. Secondary controls were exerted by water fluxes (20-80 cm/d) and toluene concentrations tested (4-46 mg/l) relative to nutrient and/or oxygen limitations. Under conditions where the oxygen concentration was near zero due to removal by toluene degradation in the soil columns, the transformation rate was sufficiently low to be insignificant relative to column residence time.

Søvik et al. (2002) undertook lysimeter trench experiments in the Gardermoen delta aquifer to study the flow of water and transport and degradation of aromatic jet fuel components (toluene and o-xylene) in the undisturbed unsaturated zone laterally adjacent to the trench. The research was driven by the need to assess risks associated with the new Oslo airport located on the Gardermoen delta sediments, Norway's largest unconfined aquifer. Two separate trenches were used that were *c*. 6 m long and monitored an adjacent unsaturated zone over *c*. 3.5m to the underlying water table. The geology comprised alternating layers of fine and coarse sands that were horizontal near surface, but dipping at depth. Twenty drip lines irrigated a plot with 20- by 20-cm release spacing and application rates of 43 mm/d. Volumetric water contents in the unsaturated zone were generally around 0.2 (of the bulk volume), but could reach 0.4 in some fine-grained layers. An initial conservative bromide tracer test indicated travel times through the unsaturated zone were around 20 d. A significant sub-horizontal displacement of the bromide plume was observed coinciding with the direction of general geological dip. Lateral migration was particularly significant along a thin dipping silty-sand layer that at least acted as a partial barrier to flow. Numerical modelling analysis by Alfnes et al. (2004a) of lateral diversion of water flow indicated anisotropy of the hydraulic conductivity within the layers was a critical

requirement in the reproduction of observed flow patterns. Capillary and hydraulic barriers were deemed to be of minor importance for the observed lateral diversion.

Søvik et al. (2002) observed the bromide plume at 3 m depth was detected at 5 m lateral distance from the surface injection point. A line-source of dissolved-phase toluene and o-xylene at 50 mg/l (and tritium as conservative tracer) was applied over 14 d with a total volume of 4200 l injected through 10 cm spaced spikes terminated at 20 cm below ground avoiding injection through the very high attenuation near-surface soil layer and volatilisation losses. These represent high concentrations and application rates, even so attenuation was very significant with very low concentrations evident 1-2 weeks after application and nearly 100 % decline in aromatic concentrations achieved within 3 m of unsaturated zone. Condition remained aerobic with first order degradation coefficients estimated at 0.2 d^{-1} for toluene and 0.1 d^{-1} for o-xylene. The research was supported by unsaturated column experiments by Breedveld et al. (1997) who observed complete removal of BTEX and naphthalene within a 1-m long column. Adaptation of the soil microflora to the applied hydrocarbons was necessary and also required when hydrocarbon application was stopped and resumed. Removal rates of 4.7 and 3.0 mg/kg/d total hydrocarbons were found for a natural mineral soil and a soil mixed with 5% peat, respectively, over the total column length. The highest removal rates (*c*. 20 mg/kg/d total hydrocarbons) were observed in the top 20 cm of the column. Observed breakthroughs over the various test runs with variable hydraulic loads (50 to 375 mm/d) were ascribed to oxygen depletion or substrate competition.

Alfnes et al. (2004b) have undertaken numerical model transport simulation of the Gardermoen dataset obtained by Søvik et al. (2002) using the unsaturated zone SWMS-3D model extended to incorporate coupled multispecies transport, microbial degradation following Monod kinetics and gas diffusive transport of oxygen and hydrocarbons. The model indicated that assumptions of homogeneous layers were too simplistic to match feild observations and sorption was reduced relative to laboratory experiments. The initial biomass and the maximum utilisation rate could be reasonably adjusted to capture the initial lag phase and overall degradation rate. Local oxygen limitation was predicted, but not observed in the field. The model predicts local oxygen demand was not significantly influenced by evaporation and diffusive gas transport. Channelling as a result of small-scale heterogeneities such as biopores was indicated to be the main cause of discrepancy between the modelled and observed behaviour.

Dror et al. (2001) also conducted controlled field experiments to evaluate the combined effect of leaching and natural attenuation on a semi-volatile kerosene petroleum hydrocarbon mixture that was applied to twelve double-ring sampling plots of 0.385 m^2 area. The site was located sandy loam on a Mediterranean Red Soil (Rhodoxeralf) located at the Volcani Center in coastal Israel. A 2 l quantity of kerosene NAPL (including 100 hydrocarbons, with carbon numbers ranging between C_7 and C_{16} and aromatics such as p-xylene and naphthalene) was spray-injected to each plot that was expected to be held as residual within 20 cm of ground surface. Plots were variously irrigated ranging no irrigation up to 500 mm, equivalent to the annual rainfall, applications in various pulse modes over a 39 day experiment period. Monitoring was via soil cores over a depth of 1 m through the unsaturated zone, aqueous-phase or vapour phase data were not measured or estimated and hence limits some of the specific interpretation. Dror et al. observed that volatilization exerted an important control on attenuation. The more soluble and therefore mobile fraction of the mixture underwent volatilization shortly after application to varying degrees depending on moisture contents. Soil-concentration profiles exhibited significant attenuation within 50-60 cm of ground surface. An initial increase in the ratio of n-alkanes relative to total hydrocarbons in the subsurface in the first leaching period was ascribed to volatilization of low-vapor-pressure compounds. The subsequent decrease of that ratio was attributed to biodegradation. The presence of some low solubility components in deeper soil layers was postulated to be due to their transport as microemulsion or by separate NAPL flow.

The redistribution of individual soluble components was in general accordance with their physico-chemical properties, leaving the heavier compounds in the upper subsurface layers.

These leaching experimental studies are also supported by studies on similar aromatic or hydrocarbon compounds principally looking at attenuation of vapours due to biodegradation (and sorption) arising from LNAPL sources, typically on the water table (Baker, 2000; Lahvis et al., 1999; Pasteris et al., 2002; Höhener et al. 2003, 2006; Gaganis et al., 2004; Broholm et al., 2005; Abreu and Johnson, 2006; Molins et al. (in press)). Such studies in general indicate that biodegradation exerts a significant control on the attenuation of hydrocarbon vapour migration that importantly would also limit the spread of aqueous-phase contamination in the unsaturated zone otherwise assisted by vapour advection and diffusion. Significant biogeochemical control on plume migration has been observed at both real sites in detail, for example the crude oil spill at the Bemidji site (Molins et al., in press), as well as research sites involving emplaced sources. One such major controlled field experiment involving an emplaced NAPL source of 13 volatile hydrocarbons (BTX aromatics, n-, iso- and cyclo-alkanes (and CFC-113 as a tracer)) was conducted at Airbase Værløse, Denmark by Christophersen et al. (2005). The site has involved a significant volume of supporting work covering NAPL source ageing (Broholm et al., 2005), changes in the microbial community (Kaufmann et al., 2004), flux measurement (Werner et al., 2005), stable carbon isotope shifts (Bouchard et al., 2008), validation of transport models (Gaganis et al., 2004) and comparison of lab-derived and field derived biodegradation rates (Höhener et al., 2006). A similar NAPL source experiment but within a large lysimeter filled with Lake Geneva sandy sediments was also undertaken by Pasteris et al. (2002) with supporting lab column and modelling studies by Höhener et al. (2003).

The field data from the Værløse site (Christophersen et al., 2005) collected over about 1 year indicate the diffusive migration of the hydrocarbon vapours was attenuation by sorption and biodegradation with concentration decline of 3 - 4 orders of magnitude to low concentrations at <0.01 mg/l (in air) within < 10 m radial distance. The 10 l volume of NAPL was positioned only 2 m above the underlying water table, but lead to minimal groundwater contamination from vapour contact (direct infiltration through the source was prevented). The experimental setup and depths to water table are not dissimilar to those used in the Borden emplaced TCE source of Conant et al. (1996) that in contrast lead to significant groundwater contamination (Rivett, 1995) and implies the comparative importance here of ready aerobic biodegradation and attenuation of hydrocarbons. Höhener et al. (2006) usefully cite the somewhat conflicting literature on biodegradation rates and kinetics controlling hydrocarbon vapour migration in the unsaturated zone that provides first-order, zero-order or Monod biodegradation kinetics rate estimates for the various systems studied. Their comparison of field-derived biodegradation rates from Værløse with various related lab studies (cited above) indicates reasonable agreements of estimates in the main with compounds of low reactivity (n-hexane, 3-methylpentane, the cycloalkanes, and isooctane) having first order rate coefficients between 0.005 and 0.35 d^{-1} and compounds with documented high reactivity (toluene, m-xylene, 1,2,4-TMB, n-octane and n-decane) having rates significantly larger than 0.35 d^{-1} with columns better predicting the field rates than the microcosm approach (uncertainty was within a factor of two or three). Lastly, n-dodecane and benzene are described by Höhener et al. (2006) as problem compounds in that they could not be assessed unambiguously. For example, for benzene the lab systems failed completely (by an order of magnitude and greater) to predict the relatively high field-observed degradation which ranged between 0.45 and 1.95 d^{-1} (depending on the model used). The field study by Pasteris et al. (2002) included similar compounds but additionally included the more recalcitrant fuel oxygenate MTBE for which a rate of <0.05 d^{-1} was determined and a conclusion drawn that it could represent a threat to underlying groundwater quality in spite of its greater potential for biodegradation under oxic rather than anoxic conditions (Schmidt et al., 2004).
Overall, the controlled field studies examining percolation of dissolved-phase hydrocarbon plumes of Søvik et al. (2002) in Norway, O'Leary et al. (1995) in Canada and Dror et al. (2001) in Israel and their supporting lab and modelling studies indicate attenuation of petroleum

hydrocarbons due to biodegradation is significant and may lead to low concentrations within a few metres (or lower) of percolation through the unsaturated zone. The ready aerobic biodegradation of hydrocarbons observed in the wealth of vapour migration studies introduced, likewise supports the expectation that the infiltration of dissolved-phase hydrocarbons plumes to the water table is not expected to be a major problem due to the high biodegradation potential of the predominantly aerobic unsaturated zone.

5.6.3 Biodegradation of chlorinated aliphatic hydrocarbons (CAHs)

In contrast, biodegradation of chlorinated aliphatic hydrocarbon (CAH) VOCs within the unsaturated zone is anticipated to be much less significant, if occurring to any significant degree in many cases. There is comparatively little unsaturated zone research relative to the hydrocarbons literature. There is, however, a wealth of CAH biodegradation research within the saturated zone (Bradley, 2003).

Within the unsaturated zone, vapour migration studies conducted on the more highly chlorinated parent compounds such as TCE focus upon the primary attenuation process of sorption (Section 5.5.2). Aerobic biodegradation would not be anticipated for these more highly chlorinated CAHs unless there was a significant supply of readily degradable primary substrate (e.g., methane, propane, butane, toluene, phenol) that may allow aerobic cometabolism by toluene-, methane- (etc.) oxidising bacteria of the CAHs as a secondary substrate via fortuitous oxidation of the bacteria by organisms expressing mono- and dioxygenases and oxygen acting as electron acceptor (Hopkins and McCarty, 1995; Alvarez-Cohen and Speitel, 2001; Semprini, 1997); Semprini et al., 2007). Aerobic cometabolism may degrade a wide range of higher and lower chlorinated CAHs (albeit excluding PCE) with degradation to carbon dioxide, water and chloride and perhaps other products such as formate, glyoxylate, trichloroethanol, dichloroacetaldehyde and chloroacetaldehyde.

There appears to be few studies on the natural occurrence of aerobic cometabolism of CAHs in the saturated or unsaturated zone although it may be anticipated to be occurring at contaminated sites to some degree where suitable conditions and a primary substrate listed exist (Freedman et al., 2001). In part this lack is due to the practical difficulty of proving these reactions as for example carbon dioxide (CO_2) products may come from a number of alternative reactions at sites and hence sophisticated inorganic and isotopic monitoring methods are required to identify relatively low CO_2 concentrations produced by these and other reaction pathways of CAHs present. Kirtland et al. (2003) did, however, evaluate biodegradation processes controlling TCE and CT (carbon tetrachloride) fate in the unsaturated zone at the Savannah River Department of Energy site, South Carolina, through isotopic evaluation of $\delta^{13}C$ of CAHs and $\delta^{13}C$ and ^{14}C of vadose zone CO_2. $\delta^{13}C$ measurements showed that cDCE was always heavier than TCE by approximately 4-12‰ indicating its degradation was significant, however, separation of the various biodegradation processes possible was difficult. ^{14}C-CO_2 were modern and suggested that plant root-respired CO_2 was dominant, nevertheless ^{14}C provided a direct measurement of complete CAH mineralization to CO_2.

Compound-specific isotopic fractionation has an expanding role in separating the various CAH biodegradation processes. For example, Chu et al. (2004) in their evaluation of TCE, cDCE and VC degradation, demonstrated isotopic fractionation measured during aerobic degradation was significantly smaller than that reported for anaerobic reductive dechlorination and hence could be used to determine whether aerobic or anaerobic degradation of VC and cDCE predominated in the field. However, isotopic fractionation effects associated with (direct) aerobic metabolic and cometabolic reactions were not sufficiently dissimilar to distinguish these processes in the field. More recent work by Abe et al. (2009) using a dual C and Cl isotope fractionation approach found that the ratio of isotope enrichment factors for C and Cl were substantially different for aerobic oxidation and reductive dechlorination of VC and cDCE again suggesting that these reaction mechanisms can be differentiated in the field.

Other emerging tools have been used to try to identify aerobic degradation occurrence and nature. For example, biomolecular approaches were used by Lee et al. (2008) examined the aerobic region of the TCE groundwater plume at the Idaho National Laboratory site. A variety of naturally occurring bacteria produce enzymes that cometabolically degrade TCE, including organisms with aerobic oxygenases. Lee et al. demonstrated, through the use of enzymatic probes (finding toluene oxygenase activity) and oxygenase gene identification, that indigenous microorganisms at the site were cometabolically active and may substantiate observations of natural attenuation of the TCE groundwater plume. In situ measurements to examine the potential for aerobic cometabolism have been performed via field push-pull tests in the saturated zone. For example, Kim et al. (2006) injected site groundwater amended with bromide tracer and combinations of propane, dissolved oxygen, nitrate, ethylene, propylene, cDCE, and TCE into existing monitoring wells and observed cometabolism to occur.

Much of the available aerobic CAH degradation literature relates to the use of aerobic cometabolism as a remediation technology that involves injection of the primary substrates above with possible bioaugmentation of and nutrient addition (Semprini et al., 2009; Connon et al., 2005). For example, early work by Hopkins and McCarty (1995) used toluene and phenol substrate injections to treat TCE and dichloroethenes in the saturated zone, these aromatic substrates being preferred over methane due to their great removal efficiency of chlorinated ethenes. Gaseous co-metabolic substrate (methane, propane, butane) are generally better suited for the treatment of chlorinated methanes and ethanes (Semprini, 1997; Semprini et al., 2007) with butane often preferred potentially due to its greater carbon content and solubility (Kim et al., 1997). Gaseous substrates lend their use to remediation of the unsaturated zone contamination directly or indirectly via for example cometabolic air sparging (CAS) whereby the gaseous substrate is injected with air (e.g. 1-4% butane in air) in sparge wells screened in shallow groundwater allowing bioremediation to be enhanced in the unsaturated zone prior to vapour extraction with an overlying soil vapour extraction system as used at the Savannah River site and elsewhere (Hazen et al., 1994; Lynch et al., 2001; Semprini et al., 2007;).

Aerobic cometabolism may represent an important mechanism for the degradation of CAHs at sites that may be easily overlooked. Frascari et al. (2006) indicate some relatively recalcitrant CAHs, such as 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), have been shown in the lab to biodegrade under oxic conditions in the presence of methane- and propane-utilizing biomasses. These workers also show vinyl chloride also served as a growth substrate in their CAH mixture experiments. Freedman et al. (2001) were likewise prompted to study the role of VC in lab microcosms based upon observations at a TCE and TCA contaminated Superfund site in California where groundwater down gradient of source areas returns to aerobic conditions with methane, ethene, VC present, a scenario potentially common at many sites VC was attenuated in the aerobic zone suggesting that it is being biodegraded. Freedman et al.'s microcosms indicated that methane and ethene acted as primary substrates for aerobic biodegradation of VC with biodegradation fastest with ethene alone (with methane shown to inhibit those rates). Hence, aerobic cometabolism of VC was suspected in the field with ethene, a product of up-gradient anaerobic dechlorination reactions, serving as the preferred primary substrate. Freedman et al. (2001) also ran microcosms with VC alone and demonstrated VC after a lag period could serve as a primary growth substrate. Further, enriched cultures were able to cometabolically biodegrade additions of cis- and trans-DCE. Hence VC as a sole substrate may play an active role in aerobic natural attenuation of DCEs.

Metabolic (direct) aerobic degradation of the lesser chlorinated CAH's that act as the primary substrate and carbon source with oxygen as electron acceptor is applicable to the less chlorinated CAHs as indicated by the above work of Freedman et al. (2001) and the earlier work of Bradley and Chapelle (1998) on riverbed-sediments. They demonstrated microorganisms indigenous to a creek, where DCE-contaminated groundwater continuously discharged were able to rapidly mineralize DCE and VC under aerobic conditions. Over 8 days, the recovery of [1,2-^{14}C]DCE radioactivity as $^{14}CO_2$ ranged from 17% to 100%, and the recovery of [1,2-^{14}C]VC radioactivity

as $^{14}CO_2$ ranged from 45% to 100%. Rates of DCE and VC mineralization increased significantly with concentration and were adequately described by Michaelis-Menten kinetics. Others have shown in aerobic environments that microbes may rapidly use cDCE (Bradley and Chapelle, 2000; Coleman et al., 2002) or VC (Hartmans and de Bont, 1992; Elango et al., 2006) as the sole primary substrate accomplishing direct aerobic oxidation of cDCE or VC as a sole carbon source. For example, Elango et al. (2006) isolated an aerobic bacterium, *Ralstonia* sp. strain TRW-1, that assimilates VC or ethene (Ee) as the sole carbon source. The estimated half-velocity constant K_m values for VC and Ee were 9.09±2.97 and 5.73±2.96 μM, respectively and were almost 3 - 10 fold higher than for other VC-assimilating *Mycobacterium* sp. The strain also degraded cDCE in mineral salts. The above provides good evidence that direct aerobic biodegradation of lesser chlorinated CAHs may be expected to occur in the unsaturated zone. Further field studies of the unsaturated zone and improved monitoring technologies to recognise the reaction are necessary to prove its existence and quantify its importance (Kirtfield et al., 2003).

The potential for anaerobic conditions developing in the unsaturated zone is much lower than for the saturated zone due to the presence of the air phase and its replenishment from air exchange at ground surface. Anaerobic biodegradation is an important for all CAHs, but particularly the higher chlorinated CAHs that may be less susceptible to aerobic – oxidation processes. The complete, or perhaps partially complete, reductive dechlorination sequence, for example from TCE to cDCE to VC to Ee, is a significant natural attenuation process at many sites in the saturated zone and may serve to mitigate or reduce impacts to receptors from migrating groundwater plumes (Maymo-Gatell and Anguish, 1999; Sherwood Lollar et al., 2001). Relatively reducing conditions are required, however, with iron/manganese-, sulphate-reducing and methanogenic conditions typically evident at sites where dechlorination pathways to ethene are complete either naturally or induced by bioremediation (Major et al., 2002). Rather than complete dechlorination to ethene/ethane, there may also be some opportunity for anaerobic oxidation of some CAHs, particularly less chlorinated compounds. For example, cDCE may be biodegraded under Mn(IV)-reducing conditions and be mineralized to CO_2 (Bradley et al., 1998), DCE and VC likewise mineralized under methanogenic and Fe(III)-reducing conditions (Bradley and Chapelle, 1997). Dijk et al. (2000) indicate these and other CAHs, e.g. 1,2-dichloroethane (DCA), may be oxidised under these and nitrate-reducing conditions in particular. Fang (2009), however, based on their recent on contaminated sediments from 9 sites in the US failed to observe anaerobic oxidation of cDCE or VC in any of the 350 microcosms used. It was hypothesised that the anaerobic oxidation observed in some sites or laboratory studies might have been due to aerobic oxidation from very low fluxes of oxygen. This accords with low oxygen thresholds reported for isolated aerobic VC-oxidizers, occurrence of oxygen-contamination reported by workers investigating anaerobic mineralization and Fang's further work where low quantities of oxygen added to anaerobic microcosms allowed aerobic VC-oxidizing mixed cultures to develop. The entry of oxygen to anaerobic zones that may develop is a significant possibility in the unsaturated zone and may likewise cause confusion over whether mineralization to CO_2 is caused by oxygen or Fe/Mn present.

Reducing conditions are unlikely to be widely present in the unsaturated zone and likely restricted to, for example, anaerobic niche zones that have locally developed unless there has been a major input of biodegradable material where reduced zones may be locally significant. These may form perhaps where natural or anthropogenic loadings of biodegradable organic matter or contaminants are significant and, or circulation of the air phase and hence oxygen entry is restricted. The latter may, for example, occur perhaps in the body of waste itself (e.g. beneath a cap that has been placed or "crust" that has developed across a waste deposit, or a "plugged" zone of the waste with accumulated fines), a low permeability, water-saturated horizon in the unsaturated zone, or a fine-grained dual-porosity aquifer matrix. Equally, such a matrix may not be accessible to bacteria due to pore throat size exclusion and cause bacteria to be largely restricted to the fracture surfaces and immediately adjacent matrix that may be expected to be

aerobic in most unsaturated zones, e.g. a sub-micron pore UK chalk matrix may fit this description (a sandstone typically would not). The most notable driver for the formation of local to moderately extensive anaerobic zones would arise in industrial – urban settings from the release of biodegradable hydrocarbons. Reducing zones in the unsaturated zone are present at most hydrocarbon release – LNAPL sites and may be moderately extensive and cover the range of biogeochemical reducing zones to methanogenic conditions. Detailed investigation of the Bimidji crude oil release provides perhaps the best real site example of the biogeochemical conditions that may be generated. CAHs entering such zones would have significant anaerobic biodegradation potential.

Although niche anaerobic zones have been postulated at some VOC-contaminated sites (Ellis et al., 1997; Kirtland et al., 2003), the evidence provided in support is not always unequivocal. For example, Kirtland et al. (2003) postulate it as an explanation for the occurrence of cDCE that is almost certainly formed from biodegradation rather than industrial inputs, however, the evidence of direct detection of those zones in the unsaturated zone is lacking. Related research on the occurrence of anaerobic niche zones in the unsaturated zone is provided by the literature on nitrate migration to groundwater through the unsaturated zone from primarily diffuse agricultural fertilizer applications of nitrate in rural area. The primary interest being to establish if such anaerobic conditions exist that may drive denitrification and reduce nitrate impacts to groundwater. Much research has been undertaken in the UK chalk and Permo-Triassic sandstone major aquifer systems summarised by Rivett et al. (2007) in this regard. The weight of evidence points to only very limited denitrification activity and hence infrequent anaerobic zones being present in these unsaturated zones. Dentirification was shown to most significant where pollutant sources were present, for example in chalk strata beneath an unlined cattle slurry lagoon (Gooddy et al., 2002). It is emphasised more reducing conditions (than nitrate-reducing) would be required for CAH dechlorination to occur. These, however, may be possible for some industrial source zones containing elevated leaching fluxes of degradable contaminant, particularly if oxygen replenishment becomes limited in the unsaturated zone.

5.7 ABIOTIC CHEMICAL REACTIONS

Chemical (abiotic) reactions causing contaminant transformation may be important for some specific VOCs (Jeffers et al., 1989; Vogel et al., 1987). The range of VOCs transformed by abiotic reactions is more restrictive than that found for biotic reactions. Where VOC abiotic reactions do occur, it may prove challenging in the field to quantify their contribution against mutually occurring biotic reactions, particularly where similar products are generated. In most environmental settings, including the subsurface water environment, the majority of chemical species that may chemically react with organic compounds are inorganic nucleophiles, for example (in order of increasing nucleophilicity), water, NO_3^-, F^-, SO_4^{2-}, CH_3COO^-, Cl^-, HCO_3^-, HPO_4^{2-}, Br^-, OH^-, I^-, CN^- and HS^- (Schwarzenbach et al., 1993). Due to the large abundance of such nucleophiles in the environment, reactive electrophiles are short-lived and organic chemical reactions with such species tend to be restricted to light-induced (e.g. atmospheric) or biologically mediated processes. Nucleophiles possess a full or partial negative charge centre and/or contain non-bonded valence electrons and will try to form bonds with electron-deficient atoms (positive charge centres) in organic contaminant molecules. Typically such bond formation will lead to a breaking of an existing bond to the atom where the reaction occurs and a group (or atom), referred to as a "leaving group", will split off leading to a transformation of the organic compound.

VOCs amenable to abiotic chemical reactions are typically chlorinated, brominated or perhaps oxygenated compounds as these electronegative "heteroatoms" will induce partial positive charge reaction centres on adjacent carbons and they may also form good leaving groups in the form of Cl^- or Br^- that are stable species in solution. Even so, many halogenated VOCs may still prove to be relatively unreactive (Butler and Barker, 1996), for example chlorinated ethenes will tend to repel nucleophiles due to the high charge density of their double bonds. Similarly, high

electron densities on aromatic ring hydrocarbons will cause BTEX and similar compounds, for example mono and dichlorobenzenes, to be unreactive abiotically. Heteroatoms located on a hydrocarbon side chain of an aromatic compound may, however, induce reactive centres on the side chain, for example $Cl\text{-}CH_2\text{-}C_6H_5$ and $Br\text{-}CH_2\text{-}C_6H_5$ have hydrolysis half-lifes (at 25^{o}C) of just 15 hours and 0.4 hours respectively due to the reactivity of the carbon adjacent to the halogen (Schwarzenbach et al., 1993).

Although water is not a potent nucleophile, it is nevertheless highly abundant and may be important for some VOCs as it represents by far the most prevalent nucleophile present in an infiltrating VOC plume. A reaction in which a water molecule or hydroxide ion (under more elevated pH conditions where reaction rates may be faster) substitutes for another atom (or group of atoms) in an organic molecule is referred to as an "hydrolysis" reaction. It is an important nucleophilic substitution reaction because the compound will be transformed to a more polar compound with a C-OH bond (e.g. an alcohol) that is typically of less environmental concern relative to the parent compound and likely more biodegradable. If the formed alcohols are halogenated, then subsequent hydrolysis to acids or diols may occur (Vogel et al., 1987). Hydrolysis and other nucleophilic reactions are typically energetically favourable and tend to proceed in one direction and are generally regarded as irreversible. Washington (1995) provides a comprehensive review of the hydrolysis of VOCs and tabulated half lives. It should be noted that VOC hydrolysis rates are sensitive to pH due to acid/base mediated reaction mechanisms (which could be important in waste disposal settings with more extreme pH wastes present) and also temperature. The latter is particularly important as the relatively high activation energies for most VOC reactions means that half lives may be more than an order of magnitude longer at 10^{o}C compared to 25^{o}C (Washington, 1995). The temperature profile of the unsaturated zone and waste repository may hence be important to consider for VOCs that are reactive.

Hydrolysis half-lives at 25^{o}C and pH 7 of many haloalkanes and halogenated alcohols are less than 100 years (yr) many halomethanes (Freon-like compounds) and halogenated aldehydes are less than 1000 yr and many haloalkenes (e.g. TCE, PCE) and aromatic VOCs (e.g. BTEX, chloro- or dichloro-benzenes) tend to exceed 1000 yr (Washington, 1995). On the timeframes of travel through unsaturated zones, it is hence the <100 yr half-live grouping that is of any significance. Half-lives less than 10 yr (at 25^{o}C and pH 7) include chloroethane, 2-chloroethanol, 2-chloropropanol and less than 1 yr (at 25^{o}C and pH 7) include 1,3-dichloropropene, 1,1,2,2-tetrachloroethane, 2,2,2-trichloroethanol, 1,1,1-trichloroethane (TCA). Butler and Barker (1996) also tabulate abiotic hydrolysis (substitution and dehydrohalogenation) half-lives at 10 to 25^{o}C for halocarbons with values around or less than 1 yr given again for chloroethane, TCA, 1,1,2,2-tetrachloroethane and additionally (to the above listing) bromomethane, pentachloroethane and bromoethane. Similar tabulations exist in Vogel et al. (1987). In general, monohaloalkanes hydrolyze the fastest with rates of about 1 month (Vogel et al., 1987) with slower rates for greater compound halogenation (often attributed to steric hindrance) and for chlorinated rather than brominated compounds that are more reactive as bromine is a better leaving group. The faster rates found for some of the increasingly more halogenated alkanes is attributed to dehydrohalogenation reactions where HX (X = Halo) is eliminated to give an alkene. Brominated compounds tend to have faster rates and greater tendency to undergo reaction with fewer halogen substituents than chlorine analogues (Vogel et al., 1987).

In terms of other nucleophiles, HS^- (or H_2S) tends be regarded as the most significant due to its reactivity and potential for occurrence in reduced groundwater environments. Evidence of HS^- substitution of alkylbromides leaked into groundwater with subsequent further reactions of the thiols or mercaptans (RSH or RS^-, where R = alky) initially formed that are even better nucelophiles leading to a whole series of dialkyl sulphides and other hazardous products including thioethers being fromed (Schwarzenbach et al., 1985). Toxicity in this circumstance was not lowered as is typical for hydrolysis reactions. As the HS^- used is often produced from sulphate reducing activity, some biotic contributions are also probable in such circumstances.

Within the unsaturated zone setting, such reactions may only be relevant where suitable anaerobic - redox niche conditions prevail that allow HS^- to be present in solution.

In contrast to the above reactions, oxidation and reduction reactions require electron acceptors and donors respectively. Generally organic compounds act as electron donors undergoing oxidation. However, due to the electronegative character of halogen substituents, halogenated organics may often behave as electron acceptors (or oxidants) and be reduced in the process. Such oxidation – reduction reactions in the subsurface environment are dominated by biological systems, i.e. the biodegradation process discussed earlier (Section 5.6). For abiotic reactions, although most chlorinated VOCs are susceptible to reduction reactions based on thermodynamic grounds, this potential appears to be rarely met except under strongly reducing conditions, and usually not without the mediation of bacteria (Butler and Barker, 1996) For example, Jafvert and Wolfe (1987) observed significant abiotic reaction rates for hexachloroethane, 1,1,2,2-tetrachloroethane, 1,2-diiodoethane and 1,2-dibromomethane in anoxic sediment sterile controls, however, losses may have been due to a combination of abiotic reactions, not just reduction. Again, such reactions are less probable in the unsaturated zones unless suitable reducing conditions develop locally.

Recent research has focused on the abiotic (and biotic) reductive dechlorination of CAHs by natural organic matter, sulphides and mineral surfaces that may act as electron donors or mediators / carriers. Most abiotic reaction research has focused upon iron-bearing minerals, including iron sulphide (pyrite), troilite, mackinawite and iron oxide minerals (e.g. magnetite) that may transform CAHs to non-chlorinated products (acetylene, ethylene, ethane) (Ferrey et al., 2004; Lee and Batchelor, 2002a,b and citations therein). PCE, TCE, CT, cDCE, 1,1-DCE have all been shown to dechlorinate abiotically. Abiotic reactions of green rust ($[FeII_{6-x}FeIII_x(OH)_{12}]^{x+}[(A)_{x/n}yH2O]^{x-}$) that may be produced in natural or engineered systems have attracted recent interest as its reactivity (pseudo first order rates) may be 3 – 8 folder greater than pyrite producing acetylene and a lack of chlorinated intermediates (Lee and Batchelor, 2002b). These type of abiotic reactions require formation of locally significant reducing zones to be important in the unsaturated zone.

In summary, although abiotic reactions of VOCs are not generally as important as biotic reactions, attenuation of some specific of the halogenated VOCs prone to either hydrolysis or dehydrohalogenation may be particularly significant in unsaturated zone environments and reduce impacts of percolating VOC plumes. These tend to be the more highly or least halogenated “end member” VOCs. In terms of application of half-live data to sites, it should be recognised, as noted by Butler and Barker (1996), that considerable discrepancies may exist in half-live data when comparing older and more recent studies due to the challenges involved in the determination of such rates for VOCs. Hence, all half-lives should be treated as approximate and original literature appropriately consulted. Abiotic reactions of petroleum hydrocarbons are unlikely. Where niche reducing conditions may perhaps develop, abiotic reductive dechlorination of CAHs may occur, particularly if the presence of iron minerals. Biotic reductive dechlorination may also be occurring in parallel.

5.8 TRANSPORT ACROSS THE CAPILLARY FRINGE

The capillary fringe at the base of the unsaturated zone contains pores that are nominally water saturated due to capillary rise under hydrostatic conditions. Varying grain size and hence pore size causes the thickness of this zone to locally vary. Temporal variability in recharge and rise and fall of the water table seasonally or even daily, may cause this zone to be quite dynamic, moving vertically with time and potentially containing bubbles or ganglia of air entrapped during fluctuations. Although fringe water is held in capillary tension, flow vertically or laterally cannot be completely discounted and would be enhanced under a recharge – percolation event where capillary water is subsumed, or a ‘packet’ of water effectively ‘shunted’ or displaced, into the underlying saturated zone and laterally flowing groundwater. Rates of assimilation will be driven by infiltration – recharge rates.

Under (near) hydrostatic conditions, VOC transport across the capillary fringe will be slow and occur via diffusion in response to the VOC concentration gradient present. The thickness of the capillary fringe and relative concentrations within a gradually percolating plume adjacent to the fringe, concentrations within the fringe water itself and the underlying mobile groundwater will each influence concentration gradients present and directions and rates of mass transfer. Such diffusion-based processes may only lead to significant solute mass flux to the groundwater (or vice versa) when the zones are relatively thin at scales of decimetres or lower. When the water table elevation fluctuates the vertical dispersion and mixing processes may lead to much higher rates of mass transfer across the fringe (Thomson et al., 1997). Control of aqueous-phase diffusion on VOC mass transport across the capillary fringe to the groundwater has been shown by McCarthy and Johnson (1993) who indicate that vertical transverse (mechanical) dispersion could be neglected in their lab-scale study. However, vapour-filled gas bubbles or ganglia arising from water table fluctuations may aid mass transport in either direction. Klenk and Grathwohl (2002) found vertical transverse dispersion values were greater in the capillary fringe than in fully saturated media because of air-filled voids in the capillary fringe which act as chambers in which vapour can move through more rapidly due to orders of magnitude greater diffusion coefficients in the air phase. Still, mass transport was relatively slow for a static water table, but may be expected to vary depending on air entrapment and connectivity that will depend on the geological permeability, porosity and the range and rapidity of water table fluctuation.

Several field-scale studies have provided data on VOC transfer across the capillary fringe. Both vapour contact with the capillary fringe and infiltration of contaminated water may contribute to these studies. Jellali et al.'s (2003) study of an emplaced 5 litre NAPL source composed of 13 hydrocarbons into the unsaturated zone of the SCERE's facility observed a flux to the atmosphere of 95% of the total (very near surface) source with only 4% of source mass transferred to the groundwater via vapour migration and contact with the saturated zone below. A "capillary barrier" effect was attributed to slow diffusion and weak dispersion across the capillary fringe and depleting vapour concentrations (and hence concentration gradients) due to ready atmospheric transfer. Transfer to groundwater was observed at a flux of 0.1 $g/m^2/d$ and may be significant. Mass transfer to the groundwater was also quantified by Bohy et al. (2006) and similarly transfer was limited by slow diffusion into the aqueous phase at the capillary fringe. Christophersen et al. (2005) studied concentrations within the groundwater arising from mass transfer across the capillary fringe. Components of the 10 litre NAPL source emplaced in the unsaturated zone were only detected to 30 cm below the water table and only during the initial 3 months of the experiment.

Although detailed monitoring of the groundwater was not undertaken during the vapour transport experiments of Conant et al. (1996) at the Borden site where two shallow sources of DNAPL TCE were installed just below ground and about 3–4 m above the water table, the impact of those sources on groundwater 550 days after removal was found to be significant (Rivett, 1995). An "interface plume" of dissolved TCE with concentrations three orders of magnitude greater than µg/l range drinking water standards was found in the uppermost 1-2 m of groundwater producing a plume >20 fold wider than the original DNAPL source and extended 120 m down gradient of the original source. This was in spite of the sources only being installed for 1 and 3 month periods (and then removed) and covered to prevent direct infiltration. The interface plume indicated a combination of vapour transport, percolation of water through the non-covered vapour plume and fluctuations in the water table (~ 1 m) caused significant VOC transfer across the capillary fringe and incorporation of VOCs into groundwater.

Where seasonal or event-driven water table fluctuations are large, then VOC concentration variation may depend on infiltration fluctuation (Thomson et al. 1997; Fretwell et al., 2005). The latter indicate this effect in the dual-porosity Chalk of Northern Europe, which is subject to large seasonal water-table fluctuations. Contaminant accumulated in the upper levels of the seasonally unsaturated zone, less accessible to groundwater, may over the long term act as a persistent source. From tracking of shallow groundwater VOC plumes by soil gas surveys, it is clear that

VOCs incorporated into the capillary fringe or shallow groundwater may also re-partition back into the air phase indicating VOC transport across this boundary may be a two-way process (Thomson *et al.* 1997; Rivett, 1995) that may be attributed to reverse diffusion gradients down gradient and weak transverse dispersion contributions. The vapour plume is hence elongated in the direction of groundwater flow as has been shown by numerical modelling studies of shallow unsaturated zone NAPL sources (e.g., Sleep and Sykes, 1989; Mendoza and McAlary, 1990; Thomson et al., 1997; Jang and Aral, 2007).

In complex source zone situations where NAPL has in fact penetrated into the capillary fringe there may still be some losses via vapour transport from such NAPL (Amos and Mayer, 2006; Cirpka and Kitanidis, 2001; Mumford et al., 2008; Roy and Smith, 2007). This occurs where a gas phase (bubble) adjacent to a NAPL source becomes contaminated by VOC vapours via gas-phase partitioning resulting in expansion of the bubble. Part of the bubble may 'snap off' and subsequently migrates upwards. This expansion process may happen repeatedly, transferring vapour mass from the capillary zone into the unsaturated zone and may lead to VOC-satuarted gas bubbles (Roy and Smith (2007); Ronen et al., 1989; Ryan et al., 2000; Williams and Oostrom, 2000). Methanogenesis can also produce supersaturated methane concentrations below the water table and methane bubbles rising across the fringe can evole other VOCs. Likewise, water table fluctuations may cause LNAPL sources on the water table to re-distribute and smear and allow enhanced vapour emissions to the overlying unsaturated zone with vapour transport facilitated by steep diffusion gradient close to the LNAPL.

5.9 RELEVANCE

Predicting the fate of dissolved-phase VOC plumes migrating through the unsaturated zone is hence shown to be a complex and challenging problem. This is due to the wide range of processes involved, i.e. advection, dispersion, sorption, biodegradation, abiotic chemical reaction that may equally affect other organic contaminants. Additionally, the processes of volatilisation from any NAPL present in the source of interest, or other sources in the vicinity and vapour-phase to aqueous-phase gas-liquid partitioning of VOCs causes significant additional complication in the unsaturated zone. Geologic heterogeneity is also important. Although the above discussion has attempted to separate out these various processes, it is clear that processes are very inter-linked, mutually influential and mutually occurring. The percolation of the dissolved-phase plume cannot be predicted, for example, without knowledge of the fate and transport of the vapour-phase VOC that may enhance or reduce the transport of a VOC plume to the underling water table.

The variable presence of the air phase, indeed, causes all the above processes to be more complex than encountered in the sub-water table saturated zone. Sorption, for example, at low water contents may be enhanced and comprise contributions from sorption at the air–water interface as well as sorption to the solid domain of the soil from aqueous phase. Biodegradation, for example, may be anticipated for VOCs that are biodegradable under aerobic conditions and has been demonstrated to be highly effective for aromatic hydrocarbons, but it much more difficult to prove for the less chlorinated CAHs, although anticipated. Attenuation of some of the more highly chlorinated CAHs is less probable, but may be possible via aerobic cometabolism if primary substrates are present or via dechlorination reactions if suitable anaerobic conditions develop. Where substantial volumes of hydrocarbons, (or other electron donors) are released, or landfill sources are producing significant methane, oxygen may be rapidly consumed as chemical/biological oxygen demands are high. Where electron donor loadings are lower, only more localised niche anaerobic zones may perhaps develop that may be difficult to prove existence of in practice. Abiotic reactions are unlikely for most petroleum hydrocarbons, but may be possible for selective CAHs under appropriate conditions. Reducing conditions are necessary for reactions with iron minerals which can occur where chemical/biological oxygen demand is high enough. The nature of the source zone may also be influential and for density-driven vapour flow to effectively "draw down" an aqueous-phase plume through advective flow and

contamination of pore waters would require the presence of NAPLs of high RVD. Overarching these complexities are the difficulties of reliably predicting advection and dispersion in heterogeneous unsaturated zone.

Some sophisticated multi-process, multi-phase numerical models have been developed to simulate VOC migration in the unsaturated zone. These have much improved capabilities relative to simple leaching models. However, they are largely still specialist research tools and need to be more widely applied to sites and scenarios to better evaluate sensitivities with respect to the prediction of VOC plume migration to an underlying water table.

6 Monitoring capabilities

This section summarises the main techniques that are available to sample and preserve dissolved phase VOCs in the unsaturated zone. The discussion does not explicitly address vapour phase or non-aqueous phase VOC sampling, which are beyond the scope of this review. Furthermore, whilst a coherent body of literature is available for vapour phase monitoring and non-aqueous phase sampling, it is apparent that sampling methods to assemble an equivalent evidence base for dissolved phase VOCs in the unsaturated zone is less mature. These limitations are attributed to the development of sampling methodologies for VOCs, which have historically been guided by studies that have focused almost exclusively on the saturated zone (Pankow and Cherry, 1996; NRC, 2005) where the risk driver was the contamination of groundwater, or the migration of vapour phase VOCs at shallow to intermediate depths where the risk driver was the vapour intrusion of building and, ultimately, impacts to human health.

The key challenges to acquiring representative samples of dissolved phase VOCs in the unsaturated zone include:

i) Sample recovery, which is principally concerned with the transfer of pore water that is either held in the pore matrix is re-mobilised under gravity during recharge events.
ii) Minimising volatile and sorptive loss, in both sampling and preservation of VOC samples.
iii) Resolution, in particular determining spatial sampling density as a function of heterogeneity in contaminant distribution.

The sampling of dissolved phase VOCs in the subsurface can be sub-divided into two methods (Silgram et al, 2003):

1) Ex-situ sub-sampling of samples recovered during drilling (soil, sediment and rock cores), where the pore water is held in the soil or sediment matrix by forces such as surface tension, capillarity, osmotic pressure and/or chemical bonds.

2) In-situ sampling from a well completion or dedicated sampling device, for which some form of energy to needs to be applied to extract the pore water.

Ex-situ sampling is typically associated with the site characterisation phase of an investigation and, therefore, provides a measure of the dissolved phase VOC at a given spatial location for a single temporal event. The results of an ex-situ study inform the conceptual site model, provide input parameters to further numerical analysis and, importantly, guide the positioning of in situ sampling locations. Whereas, in-situ sampling is associated with the monitoring phase of the investigation, where the focus is the understanding of temporal variability in specific parameters sampled at targeted spatial locations.

In practice, ex-situ and in-situ sampling methodologies share similar objectives. That is the recovery of representative pore water samples with minimal VOC mass losses. Negative bias, which results from volatile mass loss during sampling, can be as high as, or exceed, 90% in unsaturated zone sampling, depending on the method of sample collection and preservation (Couch et. al., 2000).

The following discussion summarises dissolved phase VOC sampling methods, which are available for both ex-situ and in-situ sampling.

6.1 EX-SITU SAMPLING OF DISSOLVED PHASE VOCS IN THE UNSATURATED ZONE

In principle, the techniques that are available for ex-situ sampling of VOCs in the unsaturated zone may be further categorised by the engineering characteristics of the ground, in particular

whether the subsurface zone of interest is unconsolidated or consolidated. Method selection will, therefore, be guided by the nature of the subsurface material, which may include degree of consolidation, permeability, porosity, moisture content, plasticity, stiffness, grain-size and pore-size distribution (Silgram et al, 2003; Lawrence et. al., 2006).

6.1.1 Unconsolidated samples

Sampling soils and poorly consolidated sediments for pore water extraction and VOC analysis from core samples requires sub-sampling apparatus to collect, transfer and preserve the sample. Each of the sub-sampling methodologies has differing attributes that affect the degree of negative bias in VOC measurements, associated with volatile losses. In a comparison of sampling methods, Oesterreich and Siegrist (2009) identified that sub-sampling unconsolidated core using a modified laboratory syringe or mini-coring device such as the 'Encore' sampler (ASTM, 2009.) yielded highest recovery rates when combined with immediate preservation (in methanol), whereas the lowest recovery rates were observed when samples were stored (at 4° C) without preservative for 24-48 prior to sub-sampling.

Direct push sampling devices, such as the Waterloo Profiler™ , have been applied to characterise VOC profiles in the unsaturated zone (Amos et al., 2008). VOCs in water (below the water table) and vapour (in the unsaturated zone) are collected via a small diameter bladder pump (where the gas drive is isolated from the sample recovery tubing) close to the tip of the driven probe. Pore water concentrations in the unsaturated zone are then inferred using a Henry's law partitioning calculation. The application of direct push samplers (NRC, 2005) is limited by depth (typically < 30 m) and the subsurface conditions. Direct push samplers are more typically deployed in the unsaturated zone to characterise vapour phase plumes and in the saturated zone to rapidly delineate the spatial distribution of VOCs in groundwater.

6.1.2 Consolidated samples

Rock core sampling is constrained by similar aspects of unconsolidated sampling, particularly the requirement to minimise volatile losses during the pre-analytical phase of sub-sampling.

A methodology described by Stuart (1991) preserves a 5 g sub-sample of rock in a headspace vial containing ultrapure water. The sampling and preservation methodology relies on partitioning of VOC from the pore water to the aqueous phase and subsequent analysis by headspace GCMS. An equivalent method is described by Sterling et al. (2005), where rock core sub-samples are preserved in methanol prior to headspace analysis (USEPA, 1997).

Pore water can be extracted by refrigerated high-speed centrifugation (Lawrence et. al., 2006). However, this methodology is only suitable for constituents that may have been released with the VOC, including inorganic determinands and non-volatile parameters, e.g. pH and electrical conductivity.

6.2 IN-SITU SAMPLING OF DISSOLVED VOCS IN THE UNSATURATED ZONE

Recovering representative samples of pore water held by capillary suction at depth in the unsaturated zone presents a number of challenges, not least of which is recovering sufficient volume of sample for analysis whilst minimising volatile losses. The limited number of in-situ sampling devices that can be installed in existing monitoring wells and specific installations reflect these challenges.

The following sub-sections describe two specific types of sampler. The first type is based on a porous suction sampler to directly recover pore water. The second device is deployed in existing monitoring wells and exploits phase partitioning to infer soil water composition from vapour phase VOC concentrations. Furthermore, the latter methodology has been applied to studies of VOC distribution in the region of the capillary fringe, which is a transition zone between the unsaturated and saturated zones, where pore water is held both at suction and at atmospheric

pressures, which may also be associated with steep VOC concentration gradients (Ronen, et. al.,2005).

6.2.1 Porous suction samplers

Porous suctions samplers are generally used for sampling pore water at shallow depths (Abit et al.,2008; Duke et al., 2007; Gaganis et al., 2004; Jellali et al., 2003; Lahvis et al., 2004). These samplers comprise porous cylinders, which are closed at one end and are inserted into a pre-formed hole in the soils or sediment and and sealed in using silica flour and bentonite. By applying suction to the sampler, water moves into the pot and is drawn to surface. However, the volume of the sample tube and the pressure required to lift the sample to the surface, may preclude the deployment of the sampler at depth (USEPA, 1986). A further concern of the sampling methodology is the potential for VOC mass loss due to the negative pressures applied in the sampling device.

Smith et. al. (1991) illustrate the detailed design of a closed sampling system designed to minimise volatile losses in sampling unsaturated zone pore water at the Picatinny Arsenal site and simultaneously compared four VOC analysis methods for TCE. They found reasonable agreement across the four methods. The method which utilised a simple withdrawal syringe system and purge-and trap system sampling recorded the highest TCE recoveries and proved to be the most repeatable method. Lahvis et al. (2004) also demonstrated that porous suction sampling results were reasonably comparable to measurements made in adjacent VOC vapour gas sampling probes. These combined studies suggest that, with care, reliable dissolved phase VOC data may be obtained at shallow depths from porous suction samplers.

6.2.2 Passive samplers

Passive VOC samplers provide an indirect measurement of the concentration of dissolved phase VOCs in the unsaturated zone by exploiting dialysis processes across a permeable membrane (Puls and Paul, 1997). In the unsaturated zone, the equilibrium vapour phase concentration in pore space is considered to be representative of the pore water VOC concentration, which can be calculated using Henry's law. Equilibration times are approximately 2 days (Laor et al., 2003) for vapour phase TCE in the unsaturated zone and approximately 6 days (Kaplan et al., 1991) in the groundwater.

Ronen et. al. (2005) described the use of a passive multilevel sampler to characterise the distribution of VOCs at the interface between the unsaturated and saturated zones. The sampler comprised a series of vertically stacked dialysis cells, which were separated in the monitoring well by a disc of diameter approximately equal to the inner diameter of the well. The dialysis cells were filled with distilled water, closed at either end with a 0.2 um permeable membrane and deployed at depth for a period of equilibration. The results discriminated between TCE unsaturated zone concentrations in stratified sediments with variable moisture content, which ranged between <1.0 and 16.5 %. Consecutive samples using the stacked cells with a vertical spacing of 12 cm were capable of resolving changes, from adjacent sample cells, in TCE concentration approaching 24,000 μg/L. The study concludes that active pumping from equivalent locations has the potential to mix zones of different concentration and draw vapour from zones that are not representative of the sampling zone. A disadvantage of this time-integrated sampling methodology is that the timing of contribution to total VOC mass is unknown. However, reducing the temporal monitoring frequency may reduce the uncertainty is the timing such events.

7 Application to fractured and dual porosity systems

7.1 INTRODUCTION

This section describes the behaviour of VOCs in the unsaturated zone of fractured bedrock. In dual porosity systems, the fractures (secondary porosity) that bisect the rock matrix (secondary porosity) represent only a small percentage of the overall bulk rock volume, but typically form high velocity, preferential pathways to the water table for dissolved phase VOC movement. The pore structure in the rock matrix provides a storage reservoir for VOC mass, is typified by slow migration velocities and in low permeability formations is dominated by diffusion-based transport. The processes that control both DNAPL and dissolved phase contaminant distribution in the unsaturated zone of fractured bedrock are discussed, with specific reference to the Permo-Triasic sandstones which form one of the major UK aquifers that has been impacted by VOCs from the manufacturing, storage and usage of chlorinated solvents (Tait et al, 2008).

In unsaturated fractured bedrock, NAPL can migrate both vertically and horizontally through the fracture network in the unsaturated zone. In systems where the porosity of the rock is low, or pore entry pressures are high, the majority of the NAPL movement may be contained within the fracture network (Pankow and Cherry, 1995). Where this occurs, NAPL is likely to spread over a much more extensive area both vertically (through fractures) and horizontally (through bedding parallel apertures) than would be expected from a non-fractured scenario (Pankow and Cherry, 1995). Where low pore entry pressures (large pore throat diameters) exist, the NAPL will invade the matrix and spread over a smaller volume of the unsaturated zone. Where NAPL transport is contained within fractures, matrix diffusion will cause dissolved and gaseous phase VOCs to migrate into the rock matrix from the contaminated fractures (Parker et al., 1997). VOC removal rates that are controlled by diffusion are usually rate-limited and characterised by extended remedial timeframes.

DNAPL movement in fractures has been examined in a limited number of field studies focusing on the unsaturated zone. One such site was a former gasworks in Haslev, Denmark located on clayey till approximately 10-20 m thick (Jakobsen and Klint, 1999). Excavation of the site enabled visual identification of the fractures, which were classified into 4 types. Type 1 were characteristic of glaciotectonic fractures, type 2 were sub-horizontal and dipped weakly towards the direction of the ice movement, type 3 were smaller horizontal fractures restricted to the upper 4.5 m and type 4 were irregular and undulating and are likely to be desiccation fractures. Free phase coal tar was observed in all four fracture types and flowed freely out of newly opened fractures. The path of the coal tar was through 1.5-2 m of fill, sandy diamicton with worm holes and dessication fractures, then into horizontal fractures at 2 m bgs. This area was intensely fractured, which caused DNAPL to spread laterally about 20 m from the source. DNAPL migrated from these horizontal fractures into the type 1 vertical fractures, where migration continued vertically downwards.

In fractured systems, gravity-driven infiltration will occur in vertical or sub-vertical fractures. Even in situations where the matrix saturation is low, flow still occurs in the fractures (Duke et al., 2007; Flint et al., 2001) and can reach velocities of 5 to 20 m/d and higher. Where infiltration occurs through more highly saturated fractures, flow can be 50 to 100% greater than in equivalent fractures at low saturation. These velocities will only occur in connected fractures, it is often the case that fractures are intercepted by other geologic media or plugged by infilling or precipitates, causing a variety of affects on fracture permeability. Duke *et al*. (2007) studied the behaviour of fluids between unconsolidated sediments and fractured rock. Where unconsolidated sediment overlies fractured rock, the fractured rock provides a capillary barrier with water moving into the fractures sporadically when the head above the contact exceeds the air-entry pressure of the fractures. Conversely, in exceptional cases where fractured rock overlies

unconsolidated rock, a perched water table may be present due to contrast in permeability between the contrasting geologic media. Other examples of flow variation at contacts between geologic media include lateral flow over vitric and zeolitic tuffs under densely fractured tuff (Flint et al., 2001) and perched water over low permeability sediment layers (Robinson et al., 2005). Such layers of perched water were highlighted by Nimmo et al. (2004) as possible locations where contaminants may be concentrated or diluted. It should be noted that not all rocks containing networks of differing materials have preferential flow. The clastic dikes at the Hanford site were studied extensively, but in the end were found not to act as preferential flowpaths and more importantly were deemed to slow reactive contaminants down due to the sorptive infilling sediments which included clays, along with silts and gravels (Murray et al., 2007).

The process of matrix diffusion is concomitant with fracture flow. The process of diffusion, where contaminants are transferred from fractures into the solid geologic matrix, is usually a term reserved for dual porosity systems in which the permeability of the matrix blocks is low. Matrix diffusion in dual porosity systems is a well researched area in the saturated zone (Parker et al., 1997), but less well studied in the unsaturated zone. Matrix diffusion will occur in the unsaturated zone, in addition to vaporization and dissolution into the pore water. VOC contaminants will partition into the aqueous phase, that is present as a film of water around the sediment particles, and then diffuse into the solid matrix through the connected film of water. Mortensen et al. (2004) reported matrix diffusion in a 3.3 m long unsaturated fractured clayey till laboratory experiment. Conservative tracers were added during a high flow rate and produced an early tracer breakthrough peak after 25 minutes, followed by a long tail. For a low-flow rate, a double peak was observed. The tailing and second peak were due to diffusion into stagnant areas. These effects were more pronounced for tracers with high effective diffusion coefficients. A colloid tracer showed no double peak, due to size exclusion preventing colloid diffusion into the matrix.

The potential for biodegradation in fractured rocks has been reported and appears to be dependent on the availability of resources (Geller et al., 2000; Masciopinto, 2007; Palumbo et al., 1994). Bacteria grew quickly in response to added water and nutrients in interbedded sands and silts with high carbon contents at an arid site. Similar additions to basalt, which had a low organic carbon content caused no bacterial response (Palumbo et al., 1994). Comparable results were found by Masciopinto (2007) who correlated nitrification in fractured limestone with quantity of organic carbon in the injectant water. The availability of resources which is dependent on fluid flow and distribution within fractures was found to be a significant factor affecting the ability for organisms to degrade VOCs (Geller et al., 2000). Geller op. cit. identified that bacterial growth led to the formation of biofilms, altered the liquid surface tension, locally altered permeability and redirected infiltrating liquids.

In summary, the unsaturated zone of dual porosity systems are inherently complex and are characterised by complex contaminant transport processes and infiltration rates, which vary over a range of timescales. Nimmo (2004) published a table which summarises the major features and processes relevant to contaminant transport through the fractured unsaturated aquifer at the Idaho National Engineering and Environmental Laboratory. The contamination was radioactive waste and the bedrock was basalt, however their work highlights the importance of unsaturated zone processes (both favourably and unfavourably) and their inherent complexities; an adapted version of the table is shown (Table 2). Whilst the table does not specifically reference VOC contaminants, principles are of relevance when assessing solute migration in the unsaturated zone.

Table 2. Important features and processes relevant to contaminant fate and transport waste in the vadose zone as relevant to non-VOC compounds the Idaho National Engineering and Environmental Laboratory (adapted from Nimmo et al., 2004)

Feature/process	Favourable aspect	Unfavourable aspect	Complicating factors
Thick vadose zone	Long travel times to aquifer under unsaturated conditions, much material for possible sorption	Large zone of poorly understood phenomena	Difficult to i)conduct meaningful field experiments, ii) differentiate flow processes within layers, iii) monitor dynamics of system in-situ, iv) recover sediment cores for analysis
Heterogeneity of the bedrock (basalt)	High permeability increases dilution-dispersion; dense basalt slow flow	High permeability decreases travel times	Physical processes in basalt are poorly understood, sorption properties of sediment-filled fractures have not been fully investigated
Continuous sedimentary interbeds	High density of sorption sites; low hydraulic conductivity	Enhanced horizontal spreading can take contaminants outside monitoring area	Properties may not be adequately characterised to model processes realistically
Discontinuous sedimentary interbeds	Where interbeds are present: high density of sorption sites; low hydraulic conductivity	“Holes” provide fast pathways and permit bypassing of the sorptive interbeds	Continuity is not well known, especially where well density is low
Preferential flow	Promotes dispersal and dilution of contaminants	Decreases travel time; decreases number of sorption sites to which contaminants are exposed	High degree of complexity; processes poorly understood.
Vertical heterogeneity	Slows vertical flow especially under unsaturated conditions	Enhanced horizontal spreading can take contaminants outside monitored area	Particular well completion depths influence observations of perching
Horizontal heterogeneity	Slow horizontal flow	Can preferentially direct flow to regions of high vertical conductivity	Information is difficult to obtain and little is available
Episodic large-magnitude infiltration	Contributes large input of water for dilution and dispersal	Decreases travel time	Difficult to predict; antecedent moisture conditions influence effects; generates preferential flow
Perching	Provides zone for enhanced mixing and dilution of contaminants	Enables fast horizontal transport	Extent and persistence are unknown in areas lacking monitoring wells
Solute transport	Dispersal promotes dilution and movement to any sorptive regions	Causes spread of contamination	Source term is highly uncertain
Spatial geochemical heterogeneity	Increased dispersion promotes dilution and movement to any sorptive regions	Increased dispersion increases spreading; decreased retardation	There are many sources of heterogeneity; heterogeneity exists at diverse scales
Colloid transport	Filtration processes limit colloid mobility	Allows convective transport of adsorbed chemical	Adsorptive characteristics of colloids are poorly understood.

7.2 SPECIFIC REFERENCE TO PERMO-TRIASSIC SANDSTONE

The Permo-Triassic sandstone is generally a high yielding aquifer in which regional groundwater flow is increased by localised flow though fractures. It is an important aquifer and has provided water for several large UK cities such as Birmingham, Nottingham, Liverpool and Belfast. The Sherwood Sandstone Group constitutes a major part of the Permo-Triassic sandstones and is largely of fluvial origin, deposited by braided river systems. Whilst the lithology is mainly sandstone, layers of conglomerates, siltstones and mudstones up to 1-2 m in thickness are present and cycle from coarse sandstone/conglomerate to finer grained sandstones, siltstones and mudstones (Walker and Cant, 1984). Lawrence *et al*. (2006) reported three conceptual models for the interbedded sandstone-mudstone successions in the Sherwood Sandstone Group, based on geometry, ratio of sandstone to mudstone, interconnectivity of the sandstones and lateral continuity of the mudstones. The two relevant conceptual models to their study area were a 'layer cake model' which has laterally continuous mudstone beds that restrict vertical migration of fluids and a 'jigsaw model' which contains discontinuous sandstone bodies that fit together without gaps and occasionally incorporate low permeability mudstones (Figure 6). These heterogeneity styles may result from channel deposits, which were reported by Allen et al. (1997) to be potentially continuous for tens of kilometres, as observed beneath the Irish Sea. Furthermore, such heterogeneities may result in directional flow in sandstone aquifers, which is focused in the more permeable facies. This anisotropy imparts lateral spreading of infiltrating waters in the unsaturated zone, which potentially limits the vertical migration of dissolved phase VOCs from localised areas of elevated recharge (e.g. soakaways, lagoons, drainage channels).

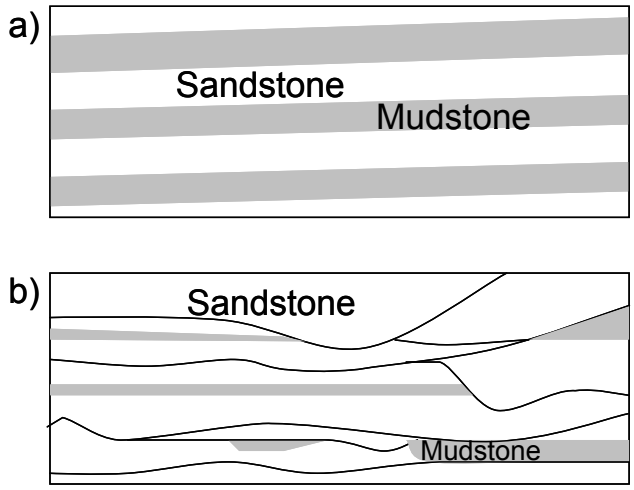

Figure 6. Models of interbedded sandstone and mudstone, a) layer-cake model and b) Jigsaw model (adapted from Lawrence et al., 2006)

The layer-cake sedimentary models provide the geological framework for field-scale solute transport models. Within each layer, hydraulic and solute transport parameters are treated as homogeneous, whilst local-scale heterogeneities within these layers such as predicting flow paths, velocity and travel times are ignored. Pan et al. (2009) studied the characteristics of both layer and local-scale heterogeneity at Yucca Mountain, to evaluate their relative effect on uncertainty in unsaturated flow and contaminant transport and concluded with four main points; 1) Layer-scale heterogeneity was more important than local-scale heterogeneity in simulating field observations of flow, hence when simulating unsaturated flow, layer-scale heterogeneity is suitable and should be calibrated using values from 3-D inverse modelling; 2) Local-scale heterogeneities only slightly change the mean predictions of percolation fluxes and tracer plumes, however they significantly increase the uncertainty of these quantities, implying that more random, complicated flowpaths are created by the local-scale heterogeneity; 3) Local-scale heterogeneity increases mean travel time for tracers in the early stage, but this effect decreases over time and 4) Layer-scale heterogeneity is more important than local-scale heterogeneity in

simulating travel time of mass to the water table. In conclusion, to decrease overall uncertainty, effort should be directed into decreasing uncertainty in layer-scale values to improe 3-D inverse model calibration.

Permeability variation in the Permo-Triassic Sandstone depends on the grain size and geometry, particle size distribution and extent of cementation (Allen et al., 1997). Layers are generally assumed to be homogeneous, but as a whole system, hydraulic conductivity is heterogeneous. Core permeametry results for the Bromsgrove Sandstone Formation found horizontal hydraulic conductivity to range from 0.02 m/d in fine–grained layers to 8 m/d in interbedded sandstone. Wide ranges are reported for hydraulic conductivity in the Permo-Triassic Sandstone around the Cheshire Basin, for example Sherwood Sandstone, 3.7 m/d (range: 10 to15 m/d); Helsby Sandstone, 3.1 m/d (10^{-4} to 15); Wilmslow Sandstone, 2.6 m/d (10^{-4} to13); Chester Pebble Beds, 2.5 ($10^{-4}$to 15) and Kinnerton Sandstone, 3.7 m/d ($10^{-5}$to 10 m/d).

The permeability of sandstone is not only due to intergranular pore space, but also the occurrence of fractures (Hough et al., 2006). Discontinuities include bedding plane fractures, inclined joints and solution enlarged fractures. The hydraulic properties of fractures within the Permo-Triassic Sandstone range from poorly permeable to highly transmissive flow paths depending on aperture, degree of interconnection and intergranular hydraulic conductivity. Allen et al. (1997) report that values of hydraulic conductivity used for regional-scale numerical modelling of the sandstone in the Cheshire and South Lancashire region, may typically be represented by a limited hydraulic conductivity range, e.g. 1-2 m/d, which reflects hydraulic conductivity values that are closer to the intergranular permeability and do not take account of interconnected fractures.

The occurrence of sediment-filled fractures has been observed in the north of England. Fractures filled with sand, clay and silts have lower permeabilities than open fractures (Hough et al., 2006; Wealthall et al., 2001). Wealthall et al. (2001) reported that sediment filled fractures would only act as preferential flowpaths when cross-cutting less permeable geologic media such as mudstone (Figure 7). Hough et al. (2006) distinguished between those filled fractures with unconsolidated and consolidated fills and concluded that sediment may be flushed out of the former, leading to an increase in transmissivity, relative to consolidated filled fractures.

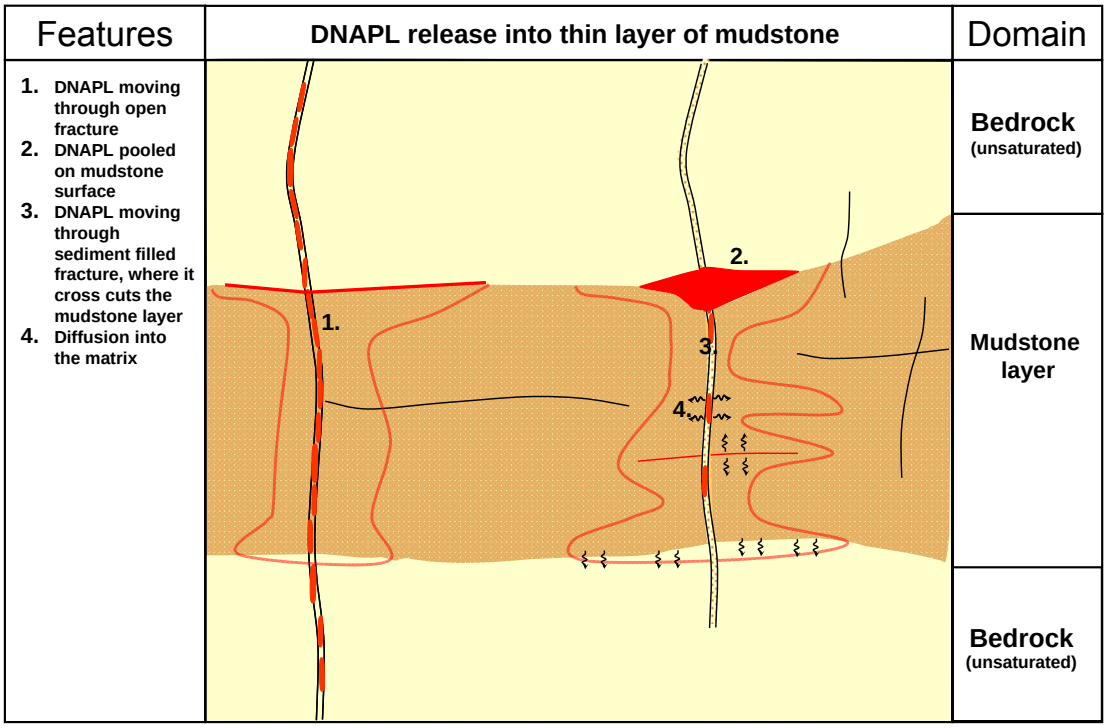

Figure 7. Conceptual model showing DNAPL transport through open and sediment-filled fractures in a mudstone layer (adapted from Kueper et al., 2003).

Transport through fractures in dual porosity systems, such as the Permo-Triassic sandstone, allows rapid migration of contaminants, relative to the matrix. A landfill site at Seisdon in Staffordshire was investigated and the leachate front was observed within only 5 m of the base of the landfill. On further investigation however, subsidiary peaks were observed several metres lower in the profile and were ascribed to rapid leachate movement through by-pass routes (Harris, 1988). Powell et al. (2003) ran a 15-month study into the transport of microbial contamination through the Permo-Triassic Sandstone and found that increased microbial counts coincided with fissures and mudstone bands. Low levels of bacteria were found even at 60 m depth, suggesting flow through preferential pathways to this depth. Determining contaminant transport in such heterogeneous systems is difficult, Stuart et al. (2006) were unable to understand the source of pesticides in Triassic sandstone in northern England, and Lawrence et al. (2006) deduced that it was necessary to take core samples on a similar scale to the heterogeneity to be ensure that the contaminant distribution could be determined accurately Morris et al. (2006) studied the movement of tracers (SF_6 and CFCs) throughout the upper 50 m of a saturated aquifer beneath a suburb of Doncaster, UK. The tracer distribution indicated modern recharge (<50 years) had penetrated to this depth. Residence time indicators suggested that the recharge was travelling through fracture systems. Similarly, a study comparing the movement of three tracers including dissolved organic matter (DOM), CFC-12 and microbial species (faecal Streptococci and S-R Clostridium) through two Permo-Triassic sandstone aquifers in the UK revealed tracer breakthrough to the groundwater (Lapworth et al., 2008). The fluorescence response of solid samples relating to Tryptophan-like intensities was highest in the centre of the depth profile; a distribution that was suggested to be due to rapid routing of recent applications of organic slurries along fractures. A similar profile was observed in samples from a multilevel sampler array, which showed tryptophan-like peaks at depths over 50 m, a pattern which was mirrored by microbial species and CFCs and was also ascribed to rapid penetration of modern recharge due to rapid fracture flow. The migration of unsaturated zone contaminants in recharge water have the potential to flow preferentially via fractures into the deeper saturated aquifer.

DNAPL transport through the Permo-Triassic sandstone is possible through the matrix as well as the fractures (Lawrence et al., 2006). Lawrence et al. (1992) simulated tetrachloroethene entry pressures required for various pore throat sizes in Permo-Triassic sandstones. It was reported that PCE heads of approximately 10 cm would be sufficient to displace the water from larger pores (10-50 μm), whilst smaller pores (1-10 μm) would require larger heads of several metres. Entry pressures with industrial grade PCE, suggest that the contact angle may be higher and hence the entry pressure lower, causing NAPL invasion into a 1 μm pore space with only 10 cm of NAPL head. Pore throat sizes were investigated in a wide range of sandstones samples by Bloomfield *et al*. (2001) in relation to DNAPL entry. Their results showed that the smallest pore throat sizes (0.1 μm) in the fine grained sandstones and mudstones, would require solvent heads of >200 m to allow invasion. Such lithologies would consequently act as a barrier to DNAPL. The entry pressures suggest that in a fractured deposit, NAPL transport could occur both through the matrix and through fractures, however, Lawrence *et al.* (2006) suggested that the matrix may be more important in Permo-Triassic sandstones because:

"-The major vertical or subvertical fracture spacing is large (10-20 m); the contaminant would be in contact with a much greater area of matrix than fracture since typically the ratio of matrix to fracture porosity is greater than 50:1

-The majority of vertical or subvertical fractures are thought to be sediment-filled which considerably reduces the permeability contrast with the matrix

-Many vertical or subvertical fractures are discontinuous and are restricted to individual beds and are therefore less than 2 m in length

-Larger pores (and fractures) will have been drained and DNAPL will migrate preferentially through these air-filled voids [30% of voids are air-filled] with a high potential for retardation"

The transport of DNAPL is complicated by the variation of parameters, such as pore entry pressures and wettability. For example, pore entry pressures have been reported to be substantially reduced in sandstone due to the presence of carbonate mineral phases within the pore space. Gooddy et al. (2002) observed the presence of calcite and dolomite in sandstone cores and found correlations between the carbonate content per unit porosity and a reduction in PCE entry pressure. One consequence of lower observed entry pressure is that solvents are likely to penetrate more deeply into the matrix of water-saturated sandstones than previously expected.

Changes in wettability properties of the sandstone can be caused by repeated exposure to mixed DNAPLs, which causes reduced entry pressures required for DNAPL entry into the rock matrix (Harrold et al., 2001).

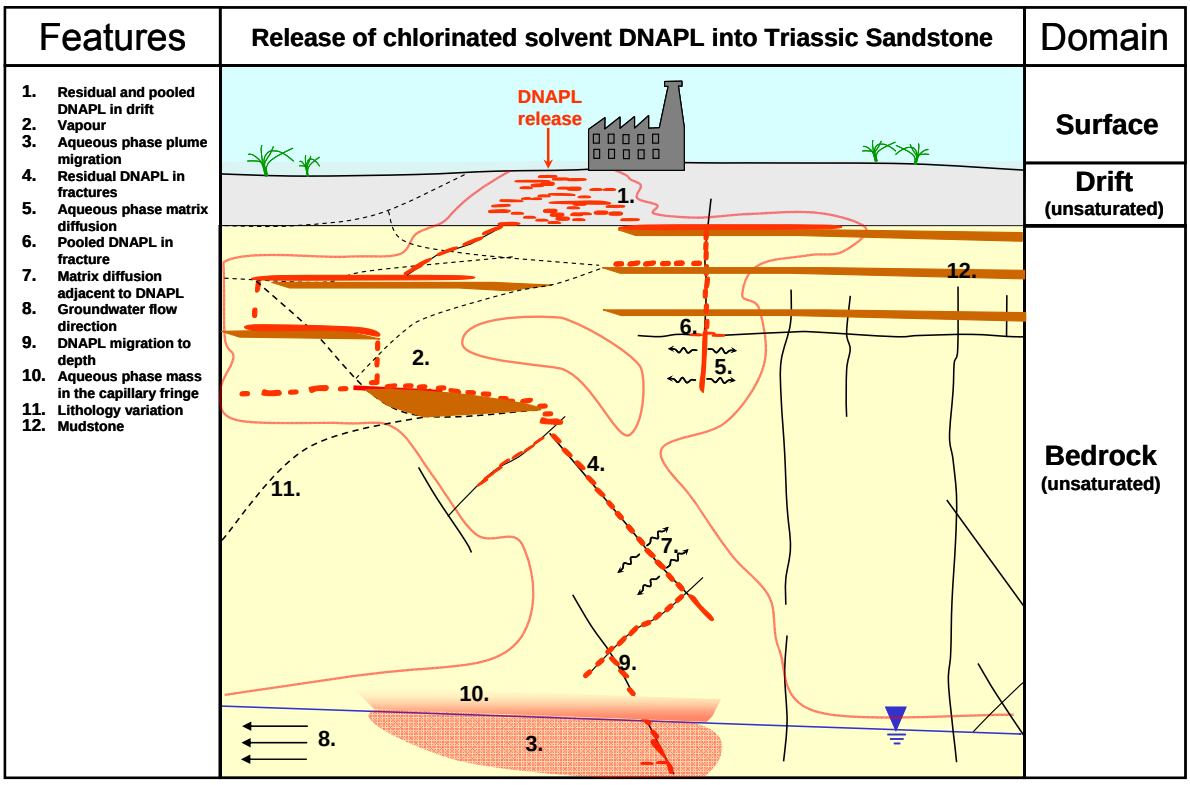

Figure 8. Conceptual model showing release of DNAPL into Triassic sandstone (adapted from Kueper et al., 2003)

Fine grained mudstones will have very high entry pressures, which will limit vertical DNAPL transport and result in lateral transport of DNAPL (Figure 8). Where the lithology is analogous to the jigsaw model (i.e. where low-permeability deposits act as baffles rather than barriers), it is likely that downward movement will occur, as NAPL can flow around the barriers. In comparison, in the layer-cake model (i.e. where distinct permeability layering occurs), NAPL will flow laterally until vertical fractures are encountered that cross cut low permeability strata. The development of such conceptual models is limited by sparse field evidence, which in turn results in uncertain models of the spatial characteristics of DNAPL source zones in unsaturated dual porosity aquifers.

Throughout the DNAPL flowpath, residual NAPL will remain for subsequent sorption, dissolution and evaporation. Lawrence et al. (2006) estimated that residual NAPL may occupy 5-10% of the bulk rock volume in Sherwood Sandstones. Lawrence et al. (2006) emphasised that the pore-throat size distribution is a key method in determining the drainage characteristics of NAPL phases and hence, the likely distribution of residual mass. In sandstones with a limited pore throat size distribution, a small increase in pressure in pressure above the DNAPL invasion pressure would simultaneously invade the pore space. However, it was also acknowledged that

the residual NAPL would also drain freely from such sediments. In comparison sandstone with broader pore throat size distributions would be invaded over wider ranges of pressure, however the resulting residual saturation would be greater.

The complex distribution of VOCs in the unsaturated zone of fractured dual porosity aquifers typically requires detailed site characterisation to determine whether the VOC has migrated in the non-aqueous or dissolved phase. Lawrence et al. (2006) suspected that VOC contamination observed in a 100 m deep cored borehole at a disused sandstone quarry, subsequently used for waste disposal, on the Runcorn Peninsula in Cheshire, was due to migration in the aqueous-phase. Their evidence included:

a) concentrations were generally below effective solubility (solubility was re-calculated to take into account multiple VOCs and salt content of water),

b) high concentrations of VOCs and inorganic ions correlated strongly, suggesting that both migrated along the same pathway. Sharp peaks of both compound types occurred at 20 and 35 m above Ordnance Datum, due to either lateral migration beneath the quarry floor on low permeability layers or fingering in fractures,

c) the ratio of TCE:PCE was constant throughout the profiles, except for the two samples with highest concentrations. The author states that if the VOCs had migrated from the quarry in the DNAPL phase the concentrations would likely have been different and considerably higher than observed. The two high concentration samples may have been associated with NAPL. As the author also points out, this could have been due to temporal variation in the composition of the waste stream.

8 Knowledge gaps, uncertainties and research needs

Although much VOC research has been conducted in the unsaturated zone, there is a lack of studies that have specifically focused on the transport and natural attenuation of dissolved-phase VOC plumes infiltrating through the unsaturated zone. Field-scale, both real sites and controlled release experiments, modelling studies and laboratory intermediate-scale tank or column experiments are required that target this scenario specifically and allow integrated assessment of the range of simultaneously occurring processes that combine to influence plume migration. This will permit key controlling processes and parameters, with the more specific process-based research indicated below, to be determined and quantified conceptual models built that may underpin more robust practitioner tools.

8.1 Processes

- *Source terms* – The VOC source term may take a variety of forms and is invariably complex spatially, temporally and in composition and is typically present as a complex mixture of chemicals with NAPL, aqueous-phase and solid phases potentially present. Most emphasis has been placed on assessing vapour migration from NAPL releases. All source types will be subject to simultaneous dissolution, leaching and volatilisation processes as well as preferential flow of both fluids that may bypass parts of the source and cause long-term tailing of the source term. There are few studies, lab, field or modelling, that have sought to address this source-term complexity, particularly simultaneous dissolution and volatilisation mass transfer and the potential for tailing. Such studies are required that allow models to be developed and validated against lab and field-scale data.

- *Advection and dispersion* – The movement of water and hence advection of dissolved solutes through the unsaturated zone is non-uniform and complex with preferential flow occurring at various scales. Understanding water movement is a research field in its own right. Dispersion of solute as a plume migrates to depth will inevitably occur within the complex flow, heterogeneous geologic regime. Most unsaturated zone dispersion measurements have been made within 2 m of ground surface and hence require up-scaling. Research into the nuances of water flow in the unsaturated zone will inevitably be continued by that research community. The critical need in the prediction of VOC plume migration is the more effective estimation of advection and dispersion occurring over unsaturated zone thicknesses in the *c*. 5 – 100 m range and whether simple rules scaling dispersion with percolation distance can be reasonably applied. Uncertainties in advection and dispersion are a handicap to determining the components of plume spreading contributed by some of the other processes outlined below and potentially lead to effective dispersion terms being developed that incorporate other plume spreading processes.

- *Water / gas phase partitioning* – Volatilisation and partitioning between the aqueous phase and vapour phase are the key processes that cause migration of VOC contaminants to be distinct from all other non-volatile contaminants. The influence is significant and may cause either more accelerated migration of a plume to a water table, or else losses of VOCs to atmosphere at ground surface and attenuation of groundwater impacts. The migration of a percolating dissolved-phase plume cannot be considered in isolation to the vapour plume. It is the influence of vapour-phase solute that may typically move more rapidly than the percolating dissolved-phase plume that needs to be better understood. Field, lab and modelling research studies could all contribute to the better understanding of the exchange of VOCs between the aqueous phase and the vapour phase and the

temporally dynamic influence of the diffusing, and potentially advecting, vapour on the overall migration of an infiltrating VOC plume to the water table.

- *Sorption* phase partitioning – Elucidation of sorption behaviour under variable water contents in the presence of air has significantly developed in recent years due to the recognition of the role that sorption to the air – water interface plays at fairly low water contents. Greater understanding of the various sorption components operating across representative water content ranges needs to be made to allow improved prediction of sorption behaviour and recognition of when simple sorption K_d approaches are likely to occur. Non-ideal sorption influences, in particular competitive sorption that may arise when a range of VOCs and other co-contaminants are present, needs to be better understood as this is a likely common scenario and may lead to reduced plume travel times.

- *Aerobic biodegradation* – Aerobic biodegradation of petroleum hydrocarbon VOCs has been shown to be very favourable mainly through vapour migration attenuation studies, but also a few aqueous-plume leaching studies. More controlled field-scale leaching studies that better quantify biodegradation rates of the biodegradable VOCs are required to increase confidence in monitored natural attenuation options for the unsaturated zone. Aerobic biodegradation of CAHs may occur by aerobic cometabolism for most CAHs and direct aerobic metabolism only for lesser chlorinated, but important, CAHs such as DCEs and VC where mineralisation to CO_2 may occur. The occurrence of these reactions is difficult to prove in the field and better methods (e.g. bio-molecular gene probe tools, isotopic tools and new methods) are required to prove occurrence and the availability of primary substrates and to quantify rates. Again controlled leaching experiments would be valuable.

- *Anaerobic biodegradation* – Anaerobic biodegradation reactions are particularly important for the VOCs that do not substantially biodegrade aerobically, nor undergo significant abiotic reaction, but may biodegrade anaerobically, e.g. many of the more highly chlorinated CAHs. An important aspect is to prove the existence of niche anaerobic zones in the predominantly aerobic unsaturated zone - to understand their character, and to evaluate their natural attenuation capacities and whether such zones may be largely by-passed by an infiltrating plume. The nature of their development and retention within say organic-rich, water-saturated, fine-grain layers, or else within high infiltration rates of high oxygen-demand organic waste effluents that may act as electron donor.

- *Abiotic chemical reaction* – Abiotic chemical reactions are only important for select CAHs under quite specific conditions, e.g. the presence of a suitable nucleophile, or the presence of some iron minerals under reducing conditions. Again the latter depend upon the appropriate development of anaerobic niche conditions that need to be understood. Where specific abiotic reactions are known to occur for particular VOCs, their rates and controls need to be established within unsaturated zone settings.

8.2 Modelling

- Various analytical and numerical models already exist of moderate to high sophistication in terms of the processes represented. Advanced numerical modelling research studies have only rarely targeted the leaching and infiltration of dissolved VOC plume scenario. The available studies deal with ‘high strength’ NAPL sources with significant vapour plumes emanating. More modelling studies should be undertaken using these codes to cover a wider range of scenarios, including lower strength source zones, than is currently reported and with a greater range of sensitivity testing.

- The advanced analytical and numerical model codes that exist have largely been used as research tools, there is a need to make these tools more accessible to the practitioner community.
- It is unclear how important observed, small-scale, non-ideal nuances (e.g. sorption variation as a function of water content, presence of anaerobic niche zones and preferential pathways) actually are and whether they require inclusion within model codes in order to provide more realistic simulations of full-scale systems. Their potential inclusion needs to be investigated and advanced modelling research tools accordingly developed.

8.3 Sampling dissolved-phase VOCs in the unsaturated zone

- A narrow range of methodologies are commonly applied to sample dissolved phase pore water in the unsaturated zone. The review identified knowledge gaps and research opportunities in novel sampling and monitoring methods for dissolved phase VOCs in the unsaturated zone. It is anticipated that a significant advance would be the development of in-situ, multi-parameter (e.g. matric potential, moisture content, water and contaminant flux) devices that report real-time data via telemetry-based instrumentation.
- Additionally, the current literature search has not identified a definitive review of sampling methods that captures all four VOC phases (solid phase, non-aqueous phase liquid, aqueous phase and vapour phase) in the unsaturated zone. A review of unsaturated zone sampling methods, for all four VOC phases, would bring together disparate literature and examples from current practice to inform future investigations of VOC contaminated sites, where pollution of the unsaturated zone is a key risk driver. It is anticipated that the aims and objectives of a state-of-the-practice review of sampling methods for VOCs in the unsaturated zone might, for example, include:
    - Objective(s) of method.
    - Characteristics of method (e.g. invasive or destructive).
    - Strengths and weaknesses of method.
    - Accuracy, precision and uncertainty issues (including issues of allowing for spatial and temporal variability).
    - Practical implications of sampling method.
    - Costs associated with sampling method.
    - Conclusions on the suitability of method, both for sampling specific determinands in the unsaturated zone and in differing geological systems.

9 Glossary

The glossary is provided for the mathematical terms used in equations in this report.

α_L	longitudinal dispersivity
α_T	transverse dispersivity
γ_n^i	activity coefficient of component *i*
λ	first order degradation rate
μ	dynamic viscosity
ρ_b	bulk density
ρ_w	density of water
ρ_o	density of DNAPL
σ	interfacial tension
θ	wetting angle
ϕ	total porosity
ϕ_w	water-filled porosity
ϕ_g	gas-filled porosity
Ψ	total potential
Ψ_g	gravitational potential
Ψ_o	osmotic potential
Ψ_p	pressure potential
$A_{ig}(\phi_w)$	water content-dependent specific surface area of the gas/water interface
c	concentration
C_g	concentration in gas (air)
C_i	equilibrium concentration
C_o^i	aqueous solubility of component m as a pure compound
C_s	concentration in solid phase
C_s^i	effective solubility
C_t	total “soil” chemical concentration
C_w	solute concentration in water
$D(\phi)$	soil water diffusivity
D_a	diffusivity in air
D_g^e	effective gaseous diffusion coefficient (gas)
D_w^e	effective gaseous diffusion coefficient (water)
D^0_a	free diffusion coefficient (air)
D_w	diffusivity in water
f_{oc}	fraction of organic carbon

g	acceleration of gravity
i	hydraulic gradient of NAPL mass
i/j	coordinate directions
K	hydraulic conductivity
K_d	partition coefficient
$K_d(C_g)$	concentration-dependent solid-water distribution coefficient
K_H	Henry's constant
K_{oc}	partitioning coefficient
m	NAPL component
n	constant
P_a^m	effective vapour pressure
P_o^m	saturated vapour pressure of component m as a pure compound
P_x	partial pressure of gas
q_w	water infiltration rate
R_g	retardation factor (gas phase)
R_w	retardation factor (water phase)
R'	redefined retardation factor r_p
r_t	pore throat radius
SA_{VOL}	porous media surface area
S_n	NAPL saturation
t	time
v	velocity
v'	effective retarded velocity
v_s	mean seepage velocity
x	distance
X_n^i	mole fraction

10 References

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